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THE NEAR ULTRAVIOLET ABSORPTION SPECTRUM OF TETRAHYDRO-NAPHTHALENE

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(Communicated by Prof. R. K. Asundi, F.A.SC.)

Abstract

The near ultraviolet absorption spectrum of tetrahydronaphthalene commonly known as tetralin consists of sharp bands in the region from 2800 to 2500 Å. The spectrum consists of about sixty bands. The maximum number of bands is obtained by using a path length of 200 cm. at room temperature which was nearly 30° C. Several of these very sharp bands have to be assigned to v–v transitions. The 0, 0 band is chosen to be at 36790 cm.$^{-1}$ Vibrational frequencies in the excited state have values 1185, 951 and 682 and combinations and overtones of these are present. Assignments of the different frequencies are discussed.

Introduction

Work on the ultraviolet absorption spectrum of tetralin in solution has been reported by Joseph Weinstock and V. Bockcheide,[15] R. A. Morton and A. J. A. de Gouveia,[7] C. S. Marvel, Ralph Mozingo and E. C. Kirkpathrick.[6] The absorption spectrum of tetralin in solution shows a peak at about 2740 Å with log E value nearly 2·8. So far no work on an absorption spectrum of tetralin in the vapour state appears to have been reported. The present work deals with this subject. The effects of temperature and increase in path length on the absorption in the vapour state have also been studied. With the help of the infra-red and Raman data[12] frequency assignments have been made and discussed.

Experimental

Tetralin is a colourless liquid with boiling point 207·2° C. The liquid was distilled and the fraction of the distillate before the boiling point was reached was discarded while the liquid distilling at the temperature corresponding to the boiling point only was taken for the experimental work. Absorption path lengths used were from 40 cm. to 200 cm. The liquid was filled in a bulb attached to the absorption tube and quartz windows were attached to both the open ends of the tube by sealing wax to carry out the experiment at room temperature. For higher temperatures varying from

30° C. to 100° C. two tubes one of 40 cm. length and the other of 160 cm. length were used. These tubes were made of pyrex glass and nichrome wire was wound over the tube. The tube could be heated to various temperatures by controlling the current by means of a variac. No windows were used and ends of the tube were open to atmosphere. There were dents provided in the tube so that the liquid could be introduced through these dents from time to time. The liquid was introduced every ten minutes and the temperature of the tube was maintained constant. The hydrogen tube prepared in this laboratory was made use of as the source for the continuum. Hilger's medium quartz and small quartz spectrographs were used to photograph the spectra with Ilford special rapid plates. Exposures of about two hours were given using Hydrogen discharge lamp and 200 cm. path length for absorption. The bands were measured by means of a Hilger comparator, copper or iron lines being used as standard lines. The wavelengths of the bands were calculated by Hartman's dispersion formula. The wavelengths of bands given in Table II represent the means obtained on five different plates and are expected to be correct to $\pm$ 3 cm.$^{-1}$ in the case of sharp bands and $\pm$ 6 cm.$^{-1}$ in the case of weak bands.

RESULTS

Tetralin absorbs in the region of 2800 to 2500 Å in solution phase. In the vapour absorption about sixty bands were obtained between 2750 to 2500 Å. At room temperature (25° C.) with a 40 cm. tube only two bands at 2717 Å and 2648 Å have been recorded (Fig. 1 *a*). As the temperature is increased to 50° C. and 70° C. the band at 2717 gets broadened while there is continuous absorption from 2717 to 2500 Å (Figs. 1 *b* and *c*). On increasing the temperature to nearly 90° C. the continuous absorption extends up to the band at 2717 towards longer wavelengths (Fig. 1 *d*). Hence a tube of 200 cm. length with sealed on windows was employed to record the spectrum at room temperature (25° C.). A side bulb attached to the tube contained a few drops of the liquid even after the tube was evacuated and sealed, the vapour pressure inside thus corresponding to the saturated vapour pressure of tetralin at 25° C. These were conditions which were favourable to bring out the maximum number of bands. A reproduction of these is given in Fig. 1 *e*. At a temperature of 70° C. and an absorption tube of 160 cm. it is observed that continuous absorption extends up to 2900 Å and that very faint bands appear on the longer wavelength side (Fig. 2). The possibility of these bands being due to an impurity suggests itself strongly on other grounds. Indeed a comparison of the wavelengths of these bands with those of naphthalene shows that within experimental

errors the values agree (Table I). It is thus very probable that the faint bands might be due to a trace impurity of naphthalene. A few of these bands are also observable in Fig. 1 *e*. The data on the observed bands together with the proposed assignments are given in Table II. The analysis is discussed below.

TABLE I

Absorption spectrum of naphthalene in vapour state

(Seshan[11])		Here	
λ in Å	ν in cm.$^{-1}$	λ in Å	ν in cm.$^{-1}$
3190	31320		
3145	31780		
3120	32020		
3085	32390	3086·6	32388
		3082·5	32431
3055	32730		
3035	32930	3037·3	32914
3015	33150	3017·1	33134
2990	33440	2989·5	33440
2975*	33640	2971·5	33643
2935	34060		
2910	34350	2911	34342
2875	34750		
2850	35100		
2820	35410		
2790	35830		
2755	36280		
2720	36750		
2690	37160		

* Probably misprint.

(Sponer and Cooper[11]) ν cm.$^{-1}$	
35780	35781
35845	35841
35920	35924
36000	35990
36395	36396
36525	36515

TABLE II

Tetralin bands 2800 *Å system*

w—weak v.w.—very weak.

λ in air A	Wave number *in vacuo* ν cm.$^{-1}$	Intensity (Visual)	Separation from (0, 0) *i.e.*, 36790 cm.$^{-1}$	Assignment
2793·3	35781	v.w.	−1009	
2789·3	35841	v.w.	−949	
2782·8	35924	3	−866	
2777·7	35990	1	−800	
2746·7	36396	v.w.	−394	
2737·8	36515	v.w.	−275	
2730·4	36614	1	−176	0−176
2727·4	36654	2	−136	0−136
2723·7	36704	3	−86	0−86
2720·7	36744	4	−46	0−46
2717·3	36790	10	0	(0, 0)
2714·0	36835	2	45	0+45
2710·5	36882	5	92	0+92
2703·5	36978	v.w.	188	
2699·6	37031	w	239	0+424−185
2696·0	37081	w	291	0+424−133
2692·6	37128	w	338	0+424−86
2689·8	37166	w	376	0+424−48
2686·3	37214	4	424	0+424
2682·8	37263	w	473	0+424+49
2679·9	37303	3	513	0+424+89
2673·6	37392	w	602	0+682−80
2670·8	37430	2	640	0+682−42
2667·8	37472	5	682	0+682
2664·6	37517	1	727	0+682+45
2661·2	37565	2	775	0+682+93
2657·9	37612	1	882	0+951−129

TABLE II—(*Contd.*)

w—weak v.w.—very weak.

λ in air A	Wave number *in vacuo* ν cm.$^{-1}$	Intensity (Visual)	Separation from (0, 0) *i.e.*, 36790 cm.$^{-1}$	Assignment
2654·9	37655	2	865	0+951−86
2651·9	37697	1	907	0+951−44
2648·8	37741	6	951	0+951
2645·2	37793	1	1003	0+951+52
2642·3	37834	3	1044	0+951+93
2638·4	37890	w	1100	0+1185−85
2635·4	37934	w	1144	0+1185−41
2632·5	37975	4	1185	0+1185
2629·0	38026	w	1236	0+1185+51
2625·9	38070	2	1280	0+1185+95
2622·2	38125	w	1331	0+1185+146
2620·2	38154	1	1364	0+1185+179
2610·2	38299	1	1509	0+951+682−124
2607·5	38339	w	1549	0+951+682−84
2604·5	38383	w	1593	0+951+682−40
2601·8	38423	2	1633	0+951+682
2598·8	38468	w	1678	0+951+682+45
2595·5	38516	1	1726	0+951+682+93
2589·2	38610	1	1820	0+951+951−82
2586·3	38653	1	1863	0+951+951−40
2583·7	38693	2	1903	0+951+951
2580·7	38737	w	1947	0+951+951+45
2577·6	38784	w	1994	0+951+951+92
2573·8	38841	w	2051	0+951+1185−85
2571·0	38884	w	2094	0+951+1185−42
2568·2	38926	2	2136	0+951+1185
2565·1	38973	w	2183	0+951+1185+47
2561·9	39021	2	2231	0+951+1185+95

TABLE II—(*Contd.*)

w—weak v.w.—very weak.

λ in air A	Wave number *in vacuo* ν cm.$^{-1}$	Intensity (Visual)	Separation from (0, 0) *i.e.*, 36790 cm.$^{-1}$	Assignment
2550·7	39193	w	2403	0+2×951+682−180
2546·9	39251	w	2461	0+2×951+682−122
2544·3	39291	1	2501	0+2×951+682−82
2541·7	39331	w	2541	0+2×951+682−42
2539·0	39373	1	2583	0+2×951+682
2536·1	39418	v.w.	2628	0+2×951+682+45
2533·8	39454	w	2664	0+2×951+682+87
2524·1	39606	1	2816	0+951+1185+682
2521·2	39651	v.w.	2861	0+951+1185+682+45
2518·4	39696	w	2906	0+951+1185+682+90
2507·3	39871	1	3081	0+951+1185+951
2501·8	39959	v.w.	3169	0+951+1185+951+88
2492·6	40106	w	3316	0+951+1185+1185

DISCUSSIONS

Tetralin (Text-Fig. 1) resembles O-Xylene in structure except that the two methyl groups in the *ortho*-position of the benzene ring are replaced by a saturated ring structure. It is observed that O-Xylene might be regarded as belonging to the group C_{2v} with two methyl groups treated as point substituents coplanar with the ring. In the case of tetralin, three more bonds

TEXT-FIG. 1

TEXT-FIG. 2

forming the ring are no longer coplanar. There is evidence to show that this saturated part of the ring is either in puckered form or the half boat form.[1,8] Thus the molecule may not be considered even to a first approximation as belonging to C_{2v} group. It may, however, be noted that the π

electron skeleton with the substituents as shown in Text-Fig. 2 essentially has a C_{2v} symmetry. Hence from the point of view of electronic structure and energy levels the molecule may be taken to belong to C_{2v} symmetry with levels suitably modified by strain in the non-planar part of the saturated ring. The near ultraviolet spectrum in the region 2750 to 2500Å corresponds to the 2550 Å band system of benzene and is attributed to transition A_1–B_1 under the reduced C_{2v} symmetry as in all other *ortho*-disubstituted benzenes. The transition is hence allowed and should show the characteristics of an allowed transition. Such a transition is expected to show a strong (0, 0) band with long progressions of totally symmetric vibrations in the excited state, the non-totally symmetric vibrations appearing mainly as ν–ν transitions. In substituted benzenes, however, this latter rule has to be slightly modified because as is generally observed the non-totally symmetric component of the 606 cm.$^{-1}$ degenerate frequency of benzene is involved more prominently than is usually expected. This feature is what many workers (Sponer and others) call the forbidden part of the allowed transition. This has been attributed to the fact that, though under reduced symmetry, substituted benzenes remember some of the characteristics of the benzene spectrum.

The near ultraviolet spectra of different O-disubstituted benzenes generally show a close similarity as far as vibrational structure is concerned. Table III records the vibrations superposed on the pure electronic transition both in the ground and the excited state of some of such molecules.

The position of the (0, 0) band is, however, determined by the general substitution effect. The spectrum of tetralin consists of sharp bands and the group of bands near 36790 to 36882 is the strongest in the spectrum. It, therefore, shows the position of the 0–0 band. It consists of a group of three sharp bands at 36790, 36835, and 36882 cm.$^{-1}$ of which the first is the strongest and the second is quite weak. Similar groups of bands are found on the shorter wavelength side separated from this group by about 424, 682, 951, 1185 cm.$^{-1}$ and combinations and multiples of these. Each of these groups consists of three bands separated by about 45 cm.$^{-1}$ A similar situation exists in the case of the near ultraviolet spectrum of O-Xylene[4] where a group of the three bands repeats itself separated from the 0–0 group at 37308 by 76 cm.$^{-1}$ The choice of the 0–0 band has obviously to be between bands at 36790 and 36882 cm.$^{-1}$ in tetralin or 37232 and about 37308 cm.$^{-1}$ in O-Xylene. In the case of O-Xylene the 37308 band has been chosen as the 0–0 band and the bands preceding it is due to ν–ν transitions. In the case of tetralin a similar choice would lead to band 36882 as the zero band and to an explanation of the two preceding bands as due to ν–ν transitions

TABLE III

Ultraviolet absorption spectra table showing the frequencies in the ground and excited state of certain O-disubstituted benzenes

O-Cresol[9]		O-Dichloro benzene[2]		O-Fluorochloro benzene[5]		O-Xylene[4]		O-Chloro Anisole[13]		O-Cl Toluene[14]		O-Fluoro Toluene[3]		Tetralin	
Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited
1261	1251	1134	1089	1246	1248	1233	1192		948		1084		1230?	(1205)R	1185
(1254)R		(1139)R		(1237)R	C.F.	(1222)R			767		1005				
1163	955	1037	958	1103	1076	1054	939	690	641		915		924	(1039)R	951
(1154)R		(1039)R		(1127)R		(1052)R		(685)R							
1040	944	662	{610	1031	929	736	692	565	518		813		707	(725)R	682
(1044)R			{640	(1029)R		(733)R		(576)R			530				
744	702	503	437	830	794	582	507	418	357					$\upsilon-\upsilon$	45
(748)R		436	307	(826)R		(582)R		(410)R		249					92
524	360	(428)		685	639			279	270	(247)					
(526)R		226	195	(680)R		$\upsilon-\upsilon$	56			161					
278	202	(240)		556	513		60			(163)					
(274)R				(554)R			72								
192	124	$\upsilon-\upsilon$	24	489	477		76								
(190)			59	(496)R			126								
				367	274										
				(375)R											
				170	99										
				(167)R											
				$\upsilon-\upsilon$	35										
					69										
					125										
0, 0 band in cm.$^{-1}$	36418	36232		37035		37308		35760		36838 Swamy		37576		36790	

separated by 45 and 92 cm.$^{-1}$ on the shorter wavelength side. But this choice has the following difficulty. It is observed that the short wavelength band, in each of the groups of three bands, is the weakest one and the longest wavelength band is the strongest. Thus in the analysis the 0–0 band would be found to be weaker than 0–2 (ν–ν) band at 36790 cm.$^{-1}$ This will also be true of subsequent groups involving 0–ν' transitions of various vibrations. Such an intensity distribution is not theoretically justifiable and therefore in the case of tetralin 36790 cm.$^{-1}$ band is chosen as the 0, 0 band. The two bands following this band at 36835 and 36882 cm.$^{-1}$ are analysed as due to transition 0–45 and 0–92. The origin of these small frequencies specially on short wavelength side of the 0–0 band is however not very clear. A similar choice of 0, 0 band could be made in O-Xylene but in this case authors always put the shortest wavelength band as stronger than that on the short wavelength side. It is significant to note that the choice of the 0–0 band does not affect the subsequent analysis since exactly a similar group repeats separated by excited state frequencies and hence the corrresponding band in each group can be chosen as the first band in the group. There are two ways in which the choice of the 0–0 band can be confirmed. Firstly the bands on the longer wavelength side involving ground state frequencies are likely to decide the choice by comparison of the ground state frequencies from *v.v.* data, with those of strong and polarized lines in Raman spectrum. Secondly the emission spectrum and the intensity distribution bands therein may decide the choice of the 0–0 band. In the present case no bands involving the ground state frequencies have been observed which can be definitely assigned to excitation of fundamentals. In the case of O-Xylene the bands specially involving ground state frequencies 1054, 1122 and 1373 support the choice of earlier workers. Having fixed the 0–0 band as the one at 36790 cm.$^{-1}$ the rest of the analysis is straightforward. On the shorter wavelength, side as has been mentioned before, there are bands separated from the 0, 0 band by 424, 682, 951, 1185 cm.$^{-1}$ and their combinations. These probably involve the excited state frequencies corresponding to the ground state frequencies 508, 725, 1039 and 1205 cm.$^{-1}$ as given by Raman spectrum. All these except the one at 508 cm.$^{-1}$ are strong bands in the Raman spectrum and possibly arise out of totally symmetric vibrations. The case of 424 cm.$^{-1}$ in the excited state will be subsequently discussed. Apart from the excited state frequency of 424 cm.$^{-1}$, the other frequencies show a behaviour very much alike other similar molecules as shown in Table II. All the *ortho*-disubstituted benzenes seem to involve the corresponding frequencies and it is interesting to note that the same trend is maintained in tetralin in spite of the ring strain.

It is interesting to note that the spectra of various O-disubstituted benzenes have one of the excited state frequency near 510 cm.$^{-1}$ There are, however, two exceptions, namely, O-dichloro benzene and tetralin. Both these compounds give bands involving a frequency of the order of 430 cm.$^{-1}$, instead of about 510 cm.$^{-1}$ The excited state frequency 510 cm.$^{-1}$ has been assigned to correspond to the ground state frequency of about 580 cm.$^{-1}$ which is the totally symmetric a_1 component of the split 606 e_g^+ degenerate frequency of benzene under the reduced symmetry. The other component is expected to be of the smaller frequency and Anno *et al.*[2] have assigned the 437 cm.$^{-1}$ excited state frequency as corresponding to 409 cm.$^{-1}$ Raman frequency which represents the β_1 component of the same 606 e_g^+ benzene vibration. In the case of tetralin the excited state frequency 424 cm.$^{-1}$ may be similarly assigned. The corresponding ground state frequency cannot be definitely identified, since no bands on long wavelength side in the region of 500 cm.$^{-1}$ from the 0-0 band could be recorded. This characteristic excitation of the a_1 component or the β_1 component of e_g^+ benzene vibration is rather significant and it may be tentatively assigned to the ring strain either by electronic forces as in O-dichloro benzene or due to steric factors as in tetralin. It may also be observed that it is likely that both may be present in the spectrum of O-fluoro-chloro-benzene[5] though the actual assignment is not very certain. This behaviour may be further studied with increasing strain as in indene, etc., where less than six-membered rings are fused to phenyl.

A few bands have been observed on the longer wavelength side of the 0-0 band. These bands, however, show a different type of appearance and are more broad and diffuse. The analysis of these bands showed that the ground state frequencies involved did not correspond to any Raman frequency. Comparison with the naphthalene spectrum shows that the strong band at 35924 cm.$^{-1}$ agrees closely with the 0-0 band of the 2500–2900 Å system of naphthalene. It is, hence, thought that the long wavelength bands may be due to naphthalene impurity. This observation is corroborated by the fact that at higher temperatures and under very long paths even the 3100 Å band system of naphthalene weakly appears on the plates. It is rather significant to note that hot bands belonging to tetralin do not develop even at sufficiently high temperatures and long columns. It is very likely that the presence of naphthalene has a part to play in this behaviour.

SUMMARY

The near ultraviolet absorption spectrum of tetrahydro-naphthalene has been studied in the present investigation. The spectrum consists of sharp bands. Vibrational frequencies in excited state have values 1185, 951 and

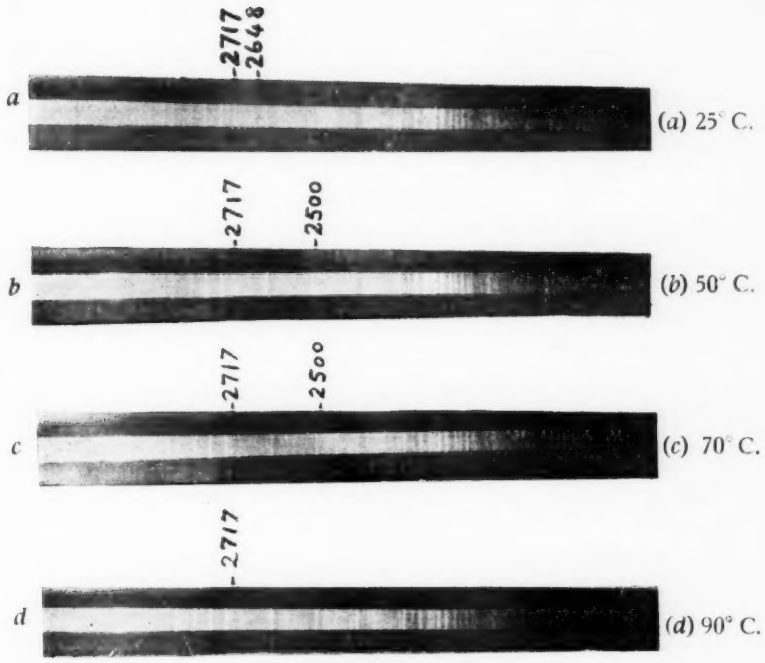

FIG. 1. Absorption Spectrum of Tetralin 40 cm. tube.

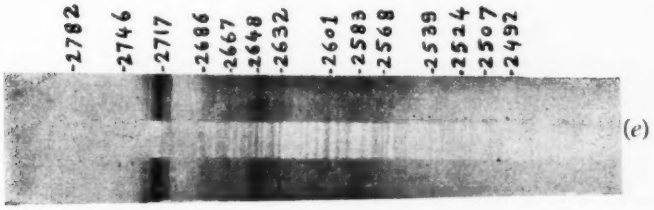

FIG. 1 (*e*). Absorption Spectrum of Tetralin 200 cm. tube.

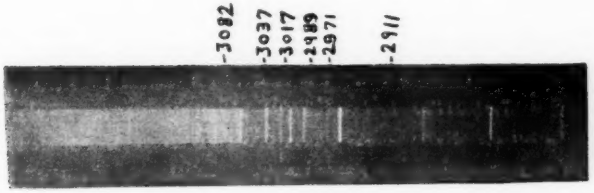

FIG. 2

682 and combination and overtones of these are found to be present as discussed in the analysis. The spectrum appears to be similar to that of O-Xylene and the frequencies in the ground and excited state of certain O-disubstituted benzenes have been compared with those obtained in tetralin.

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ABSORPTION SPECTRA OF SUBSTITUTED THIANAPHTHENES

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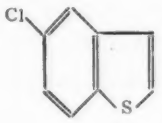
Introduction

The near ultraviolet spectrum of thianaphthene has been recently investigated by a number of workers.[1, 2] Such a study is important from the point of view of isosteric substitution of –S– in place of –CH = CH–. The derivatives of thianaphthene have been studied by Desai and Padhye[3] in solution phase. The vapour absorption of thianaphthene does not seem to have received much attention except for 3-chlorothianaphthene.[4] In the present studies it is proposed to investigate the vapour spectra of thianaphthene derivatives from the point of view of effect of substitution at different positions in thianaphthene nucleus. The substituents in the phenyl part of the thianaphthene nucleus are expected to be more interesting from the point of view of comparison with corresponding naphthalene derivatives. Absorption spectra of 5-chlorothianaphthene (I) and 7-bromothianaphthene (II) are reported here.



(I)

(II)

Experimental

The substances were obtained from Dr. Tilak of this Department and were analytically pure. An all-quartz absorption cell 33 cm. of length was used. A drop of the substance under investigation was put into the cell which was evacuated until the liquid practically disappeared when the cell was sealed off under vacuum. Spectra were photographed on a Hilger medium quartz spectrograph using a hydrogen arc as the source of continuous radiation and Kodak B–10 plates. Spectra were recorded for a range of temperatures of the cell between 30° C. and 120° C. The temperatures were increased in steps of 10° and absorption spectra were recorded until the

discrete absorption bands merged into a continuum with a cut off on a longer wavelength side. The time of exposure varied between 30 m. and 1 hour. Three plates were measured for each of two substances on a Hilger Comparator with least count ·0001 cm. Hartman's formula was used to calculate the wavelengths of the bands employing copper lines as standards.

Results

5-Chlorothianaphthene.—The spectrum of 5-chlorothianaphthene resembles closely in general appearance that of thianaphthene. The longest wavelength region of bands lies between 3050 and 2800 Å corresponding to longest wavelength absorption region of thianaphthene vapour (3000 and 2700 Å). The bands represent a typical group pattern as in thianaphthene, due possibly to a small difference frequency arising out of v–v transitions. The bands in each group show, however, a gradual fall in intensity from violet to red end as against alternation of intensity of components of each group observed in the case of thianaphthene. The second region of absorption starts at about 2700 Å and extends upto 2500 Å corresponding to second region of absorption of thianaphthene between 2650 and 2450 Å. It consists of a few broad diffuse bands. Figure 1 *c* gives reproduction of a typical plate.

The longest wavelength system consists of a number of discrete bands degraded towards the red. Some twenty prominent bands have been measured and the intense ones are given in Table I. The strongest band on the long wavelength side at 33053 cm.$^{-1}$ has been taken as the 0–0 band. The spectra recorded at higher temperatures confirm this choice since there is no reversal of intensity in the first two bands and no further bands are developed on the longer wavelength side. The electronic transition giving rise to the bands thus shows a red shift of 1009 cm.$^{-1}$ from that in thianaphthene. The vibrational assignments of these bands are given in Table I. The bands separated by 714, 1029 and 1192 from the 0–0 on the shorter wavelength side mark the beginning of separate groups and represent excited state frequencies of the prominent vibrations excited. Other vibrations involved are 626, 995 in the excited state but the bands corrsponding to these lie in the groups following the bands in the previous group. It is important to note that the vibrations which are prominently excited are those which give rise to diffuse bands or (') series in thianaphthene.[2] Excited state frequencies in thianaphthene which give sharp bands and start a group are not so prominent in the spectrum of 5-chlorothianaphthene. The bands near the 0–0 band show that one or possibly two fundamentals are excited in the ground state namely 80 and 138 cm.$^{-1}$ The bands, involving these

TABLE I

5-Chlorothianaphthene

Band heads of prominent bands

Wavelength A.U.	Wavenumber in cm.$^{-1}$	Intensity visual	Assignment	
			Ground state	Excited state
3037·2	32915	8	138	..
3031·9	32973	8	80	..
3024·6	33053	10	..	0–0
2974·3	33611	6	..	558
2968·3	33679	6	..	626
2960·6	33767	7	..	714
2936·2	34048	6	..	995
2933·2	34082	7	..	1029
2919·3	34245	5	..	1192
2888·1	34615	2	..	1562
2874·6	34777	2	..	1724

vibrations in the ground state at 32973 and 32915 cm.$^{-1}$, show a type of appearance distinctly different from the bands belonging to the group following the strong band. The group character in the spectrum of 5-chlorothianaphthene has not been well developed and hence small frequency differences for consecutive bands in each group cannot be established.

7-Bromothianaphthene—The absorption spectrum of 7-bromothianaphthene shows a characteristic difference in appearance from that of 5-chlorothianaphthene and thianaphthene itself. The longest wavelength region lies between 3050 and 2850 Å corresponding to longest wavelength absorption region of thianaphthene vapour between 3000 and 2700 Å. The second region of absorption starts at 2700 Å and extends upto 2350 Å,

corresponding to second region of absorption of thianaphthene (2650 to 2450 Å). It consists of a few broad diffuse bands.

The long wavelength system consists of a number of discrete bands degraded towards the red. Some thirty bands were measured and the prominent strong bands are recorded in Table II. The strongest band at 33493 cm.$^{-1}$ has been chosen as 0–0 band on the same grounds as in 5-chlorothianaphthene. This shows red shift of 369 cm.$^{-1}$ from the 0-0 band in thianaphthene spectrum. The vibrational assignment of these bands is given in Table II. Figure 1 *b* gives a reproduction of a typical plate.

TABLE II

7-Bromothianaphthene

Band heads of prominent bands

Wavelength A.U.	Wavenumber in cm.$^{-1}$	Intensity visual	Assignment
2984·8	33493	10	0–0
2971·6	33642	0	149
2938·7	34019	5	526
2918·6	34253	6	760
2900·6	34465	9	972
2895·1	34529	4	1036
2881·7	34692	8	1199
2875·5	34766	7	1273
2865·6	34886	3	1393

The band at 34465 cm.$^{-1}$ on the shorter wavelength side is the next prominent band in the spectrum after the 0–0 band. This involves frequency of 972 cm.$^{-1}$ in the excited state. The other excited state frequencies which could be easily identified are 760, 526 and 1273 cm.$^{-1}$ The three other frequencies which seem to be involved are 1199, 1036 and 1393 cm.$^{-1}$ In thianaphthene the difference in intensity of the v–v bands from the superposed 0–1 bands, which follow them, is quite marked and hence the excited state frequencies can be easily identified. In the present case the

whole spectrum looks like a series of bands of nearly equal intensity and hence bands arising out of 0–1 transition involving excited state frequency of some particular vibrations cannot be identified on intensity considerations alone. The identification of such bands in the present case is therefore based on the analysis, and comparison of spectra of other thianaphthenes. The difference in diffuse and sharp bands in the spectrum of 7-bromothianaphthene is not very marked. The small difference frequency possibly arising out of ν–ν transition giving rise to consecutive bands in each group in the present case is of the order 39 ± 2 cm.$^{-1}$ There are two bands at 33642 and 33345 cm.$^{-1}$ separated by 148 cm.$^{-1}$ from the 0–0 band on either side. These possibly represent the fundamental frequencies in the ground and the excited state.

DISCUSSION

5-Chlorothianaphthene and 7-bromothianaphthene are the derivatives of thianaphthene obtained by replacing hydrogen at 5th and 7th positions in the phenyl part of the thianaphthene molecule by chlorine and bromine atom respectively. In spite of this substitution the molecules retain the two symmetry elements of thianaphthene namely the plane of the molecule and the identity characteristic of a molecule belonging to a Cs group. The spectra therefore correspond to an allowed electronic transition A^1–A^1.

It has not been possible to give a complete vibrational analysis of all the bands measured for lack of adequate Raman and Infra-red data. Yet, a comparison of the prominent excited state frequencies involved in the spectra of these two molecules with those of 3-chlorothianaphthene and thianaphthene will be of interest. The results are tabulated in Table III.

Comparison of various excited state frequencies shows that all the substituted thianaphthenes show frequencies corresponding to 735, 938, 1012 and 1180 of thianaphthene. The spectrum of 5-chlorothianaphthene does not show any frequency corresponding to 1336 of thianaphthene and that of 7-bromothianaphthene possibly has the corresponding one as 1273 cm.$^{-1}$ Similarly the frequencies corresponding to 672 cm.$^{-1}$ in thianaphthene do not seem to be present in the spectra of 5-chloro- and 7-bromothianaphthene. These two frequencies seem to be predominately perturbed by substitution in phenyl part and hence possibly involve vibrations involving the phenyl part of the molecule. Hence, it seems unlikely that the 1331 cm.$^{-1}$ frequency of thianaphthene is either a C–S or C–C five-membered ring vibration. It is likely that such a mode may be associated with the frequency 1012 cm.$^{-1}$ in thianaphthene and corresponding ones in the derivatives. The frequencies

714 in 5-chlorothianaphthene and 760 in 7-bromothianaphthene correspond to the totally symmetric a_{1g} vibration 710 in naphthalene. The totally symmetric C–C vibration frequencies 938 and 1180 in thianaphthene are modified to 968 and 1213 in 3-chloro thianaphthene, 995 and 1192 in 5-chlorothianaphthene and 972 and 1199 in 7-bromothianaphthene.

The excited state frequency 626 cm.$^{-1}$ in 5-chlorothianaphthene may be due to a totally symmetric C–Cl vibration. The corresponding frequency in *para*-chloroanisole has been identified by Rao[5] as 621 in the exicted state.

TABLE III

Identified frequencies in thianaphthene and its derivatives

Thianaphthene	3-Chloro-thianaphthene	5-Chloro-thianaphthene	7-Bromo-thianaphthene
..	..	80	..
165	177	138	149
236	..	..	..
..	..	..	526
..	..	626	..
672	680	..	..
735	763	714	760
938	968	995	972
1012	1025	1029	1036
1180	1213	1192	1199
1336	1321	..	1273
1410	..	..	1393

The excited state frequency 526 in 7-bromo possibly represents totally symmetric C–Br vibration. The C–Br stretching frequency has been identified by Krishnamachari[6] in *ortho*-, *meta*-, and *para*-fluorobromobenzene as 599, 607, 513 respectively. The frequency 149 represents C–Br planar bending vibration.

TABLE IV

Comparison of positions of 0–0 *bands*

Molecule	Wavenumber of 0–0 band in cm.$^{-1}$	Shift towards Red in cm.$^{-1}$
Thianaphthene	34062	..
3-Chlorothianaphthene ..	33733	329
7-Bromothianaphthene ..	33493	369
5-Chlorothianaphthene ..	33053	1009

The characteristic difference in the relative importance of the different vibration in 5-chloro- and 7-bromothianaphthene as compared to thianaphthene is rather significant. The 5-chloro prominently shows the vibrations responsible for (') series in thianaphthene whereas 7-bromo shows those for the inprimed ones. The primed bands in thianaphthene were explained as due to those vibrations which become totally symmetric under the reduced Cs symmetry of thianaphthene (from the D_{2h} of naphthalene). It may be noted that 5-chloro corresponds to β-substitution in naphthalene and 7-bromo to α-substitution. It would be interesting to investigate the relative importance of the totally and the non-totally symmetric vibrations in the vapour absorption spectra of α and β halogenated naphthalenes.

The shift in the 0, 0 band in the spectra of substituted thianaphthenes are tabulated in Table IV. It is observed that in 3-chloro and 7-bromo thianaphthene the shift of the 0, 0 band is small and of the same order. 5-Chlorothianaphthene, however, shows a pronounced long wavelength shift. This observation substantiates the finding in the case of solution spectra of these compounds by Desai.[7] As already mentioned, position 5 in thianaphthene corresponds to β-position in naphthalene, whereas position 7 and possibly position 3, in thianaphthene, correspond to the α position in naphthalene. That β-substituted naphthalenes principally shift the long wavelength band is well recognised and hence in an isosteric molecule like thianaphthene a similar behaviour is observed. It seems, however, that the 2500 Å band system of 7-bromothianaphthene does not show the enhanced shift over 5-chlorothianaphthene as the α-substituted naphthalene would do against a β-substituted one. Hence it seems that as far as the effect of

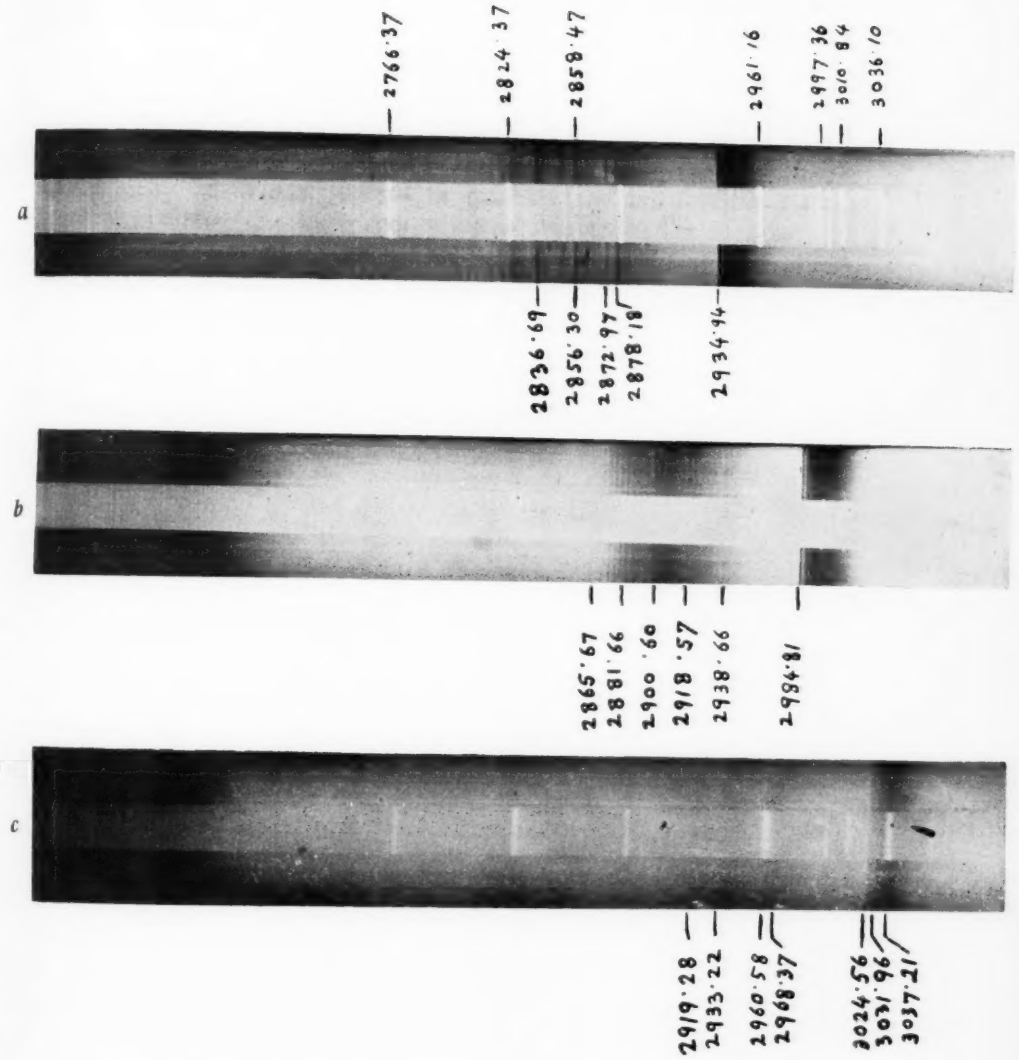


FIG. 1. (*a*) Absorption Spectrum of Thianaphthene, (*b*) Absorption Spectrum of 7–Bromothianaphthene, (*c*) Absorption Spectrum of 5–Chlorothianaphthene.

substitution on individual transitions in the spectra is concerned, thianaphthene and naphthalene show differences and each molecule has to be treated independently.

Summary

The near ultraviolet absorption spectra of 5-chlorothianaphthene and 7-bromothianaphthene have been investigated in the region 3050 to 2800 Å and 3050 to 2850 Å respectively—corresponding to longest wavelength system. The tentative vibrational assignments are put forward for the prominent bands. The assignment of certain frequencies are discussed with respect to the effect of substitution (Cl or Br) in the phenyl part of the thionaphthene nucleus.

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RAMAN SPECTRUM OF CRYSTALLINE TRI-GLYCINE SULPHATE $(NH_3.CH_2.COO)_3H_2SO_4$

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1. Introduction

In continuation of the work on the Raman spectrum of α-glycine (Krishnan and Balasubramanian, 1958), the authors have undertaken a systematic study of the Raman spectra of its derivatives. The present paper describes the results obtained with a single crystal of tri-glycine sulphate.

Tri-glycine sulphate is one of the few crystals which exhibit ferro-electricity at ordinary temperatures (Matthias *et al.*, 1956). Its transition temperature is in the neighbourhood of 48° C. The dielectric and thermal properties of this crystal have been studied in detail by Hoshino *et al.* (1957). The crystal is ferro-electric with low coercive field and has a simple domain structure. It appears therefore to be a very promising substance for use in memory devices of computers. The investigation of its Raman spectrum* and its variation with temperature would therefore be of very great interest. As it is transparent to the ultraviolet radiation, λ 2536·5 radiation could be used as exciter. Accordingly we started the investigation on its Raman spectrum. When the temperature variation of the Raman spectrum of tri-glycine sulphate was in progress, a short communication on the Raman spectrum of the same substance at room temperature by Taurel *et al.* (1958) appeared in *Comptes Rendus*. It was therefore considered desirable to publish immediately the results independently obtained by the authors at room temperature.

2. Experimental

Fairly large and clear crystals of tri-glycine sulphate were easily grown by the method of slow evaporation from aqueous solutions containing stoichiometric proportions of the two components, glycine and sulphuric acid. Crystals grown from solutions were colourless and were in the form of thick plates (about $1'' \times 1'' \times \frac{1}{4}''$) with the broad faces parallel to the *b*-axis (two-fold axis). They had only one cleavage face which is perpendicular to the *b*-axis. λ 2536·5 excitation was used to record the Raman

* The authors are grateful to Dr. K. Vedam for drawing their attention to the importance of this crystal.

spectrum. It was found that on exposure to the ultraviloet radiation for about half-an-hour the face of the crystal adjacent to the arc got frosted and the transparency decreased. This was a disturbing effect which was got over by polishing the crystal every half hour. Some specimens of the crystal got slightly coloured yellow after prolonged exposure. Using a Hilger medium quartz spectrograph and a slit width of 0·025 mm., a very intense spectrogram was obtained with the exposure of 5 hours. The illumination was normal to the broad face of the crystal plate and the scattered light was taken through one of the edges in a direction which was inclined at angle 45° to the *b*-axis.

3. Results

An enlarged photograph of the Raman spectrum of tri-glycine sulphate taken with a medium quartz spectrograph is reproduced in Fig. 1 *b* in Plate XVII. The corresponding microphotometer record is shown in Fig. 1 *c*. The spectrum of mercury arc is also included for purposes of comparison (Fig. 1 *a*). The positions and frequency shifts of the Raman lines are marked in the microphotometer record.

The spectrum recorded here exhibits 48 Raman lines. The frequency shifts of these are listed in Table I. Visual estimates of the intensities of the lines are also given within brackets in the table. Taurel *et al.* (1958) have reported only the existence of 36 Raman lines the frequency shifts of which are given in the same table. All the lines recorded by them except the frequency shift 131 have been confirmed and it is gratifying to note that in the majority of cases, the values of the frequency shifts are in very good agreement with those obtained by the present authors. The two low frequency lines 63 and 73 are not seen well resolved in the picture taken with medium quartz spectrograph (Fig. 1 *b*). In order to establish their doublet nature, the spectrum was photographed with the Hilger El large quartz spectrograph and the microphotometer record of a lightly exposed spectrogram is reporduced in Fig. 2. The two lines are clearly seen well separated not only on the Stokes side but also on the anti-Stokes side. The 63 line is broader than the 73 lines indicating thereby that the former might have a structure. The Raman line 610 and 1009 which have also been reported by Taurel and others fall adjacent to the mercury lines in the spectrogram taken with the $\lambda 2536{\cdot}5$ excitation. The Raman spectrum exhibits an intense continuous band starting from 3100 $cm.^{-1}$ and extending over 200 $cm.^{-1}$ exhibiting 3 maxima at about 3150, 3230 and 3270 $cm.^{-1}$ There is also a weak band covering the region from 2874 to 3022 $cm.^{-1}$ The frequency

shifts of the Raman lines of crystalline glycine reported by the authors recently (Krishnan and Balasubramanian, 1958) have also been given in Table I.

TABLE I

Tri-Glycine Sulphate			α-Glycine	Assignment
Sl. No.	Authors	Taurel *et al.*	Authors	
1	45 (6)	45		Lattice
2	63 (10)	64	53	,,
3	73 (10)	73	74	,,
4	102 (10)	100	109	,,
5	129 (5)	128		,,
		131		
6	171 (8)	170	164	,,
			183	
7	220 (4*d*)	207	199	,,
8	330 (6*d*)	330		C–C bending
9	345 (2)		358	C–C bending
10	450 (10)	450		SO_4^-—ν_2
11	463 (6)	463		SO_4^-—ν_2
12	500 (6)	499		C–CO bending
13	587 (3*d*)	578	588	C–CO bending
14	610	615		SO_4^-—ν_3
15	629 (6*d*)	623		SO_4^-—ν_3
16	665 (6*d*)	664		SO_4^-—ν_3
			677	
17	697 (1)		697	O–C–O bending
18	870 (10)	870		C–C Stretching
19	890 (12)	890	896	C–C Stretching
20	902 (8)	917	925	C–C Stretching
21	980 (20)	976		SO_4—ν_1
22	1009	1009		
23	1037 (1)	1037	1038	C–N Stretching
24	1043 (6*d*)	1042		SO_4^-—ν_4
25	1092 (3)			SO_4^-—ν_4
26	1114 (8)	1110	1112	$C–CH_2$ rocking
27	1134 (3)		1140	
28	1164 (4*d*)			SO_4^-—ν_4
29	1303 (10*d*)	1305	1320	C–H Wagging and
30	1321 (10*d*)		1330	Twisting
31	1375 (3*d*)	1377	1395	Symmetric Valence of $-C\langle O \rangle O$
32	1414 (15)	1405	1414	
33	1441 (12)	1435	1441	C–H Scissoring
			1459	

TABLE I (*Contd.*)

Sl. No.	Tri-Glycine Sulphate Authors	Tri-Glycine Sulphate Taurel *et al.*	α-Glycine Authors	Assignment
34	1483 (6)	1478	1506	Symmetric N–H bending
35	1609 (10)	1603	1563	C=O (ionised carboxyl)
36	1648 (5)		1640	Asymmetric N–H bending
37	1675 (10)	1678	1668	C=O (ionised carboxyl)
38	2528 (1)		2530	N–H Stretching NH_3^+
39	2651 (3)		2630	,,
40	2763 (4)		2750	,,
41	2874 (5*d*)		2830	,,
42	2930 (5*d*)		2895	,,
43	2962 (13)	2959		C–H Stretching
44	2988 (15)	2983 3012	2974	,,
45	3022 (13)	3019	3008	,,
46	3150 (6*d*)	3160	3145	N–H Stretching
47	3230 (5*d*)			—O.....H—
48	3270 (4*d*)			Hydroxyl Group

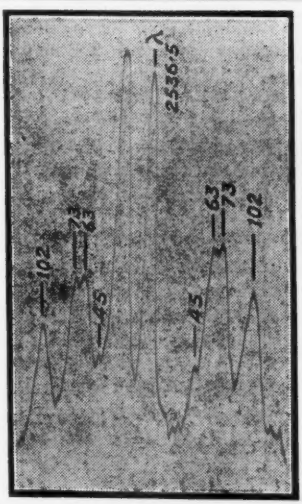

FIG. 2. Microphotometer record of the Raman spectrum (lathic region) of tri-glaycone sulphate taken with E.I. Spectrograph.

4. DISCUSSION

Tri-glycine sulphate crystallises in the monoclinic class with the space group $C_2^2-P2_1$. The crystallographic data have been determined by Wood and Holden (1957) and by Hoshino, Okaya and Pepinsky (1958). According to the latter group, the unit cell has got the following parameters $a = 9{\cdot}417$ Å, $b = 12{\cdot}643$ Å, $c = 5{\cdot}735$ Å and $\beta = 110° 23'$. The unit cell contains two molecules of tri-glycine sulphate situated symmetrically with respect to one another about the binary axis. There is no other element of symmetry at room temperature.

The observed Raman lines could be classified under 3 groups: (1) low frequency or lattice spectrum consisting of 7 Raman lines, (2) spectrum of the SO_4 ion consisting of 9 Raman lines and (3) spectrum of the internal oscillations of the glycine ion consisting of 32 Raman lines.

5. LATTICE SPECTRUM

Taking each glycine group as a unit and the SO_4 ion as another unit, one can work out the number of lattice oscillations on the basis of group theoretical analysis. The low frequency spectrum of tri-glycine sulphate should consist of 18 oscillations of the rotatory type and 21 oscillations of the translatory type, all of them being active in Raman effect. In actual practice this number may be reduced since in each molecule there are 3 units of glycine and consequently the frequencies of some of the oscillations may be nearly equal. Further, the oscillations of the rotatory type may be expected to appear strongly in the Raman spectrum. Only 7 lattice lines have been recorded in the spectrum of tri-glycine sulphate in the region from 45 cm.$^{-1}$ to 220 cm.$^{-1}$ Of these the prominent ones are 63, 73, 102 and 171 cm.$^{-1}$ The weaker lines are generally broader than the intense lines. In order to give proper assignments to the lattice lines, further investigations under high dispersion and for various orientations have to be carried out.

6. SO_4^- FREQUENCIES

From a comparison of the Raman lines observed in the spectra of tri-glycine sulphate and glycine (Table I), the following frequency shifts could be assigned to the internal oscillations of SO_4^- ion: 450, 463, 610, 629, 665, 980, 1043, 1092 and 1164 cm.$^{-1}$ Since 9 lines have been recorded, it follows that in crystalline tri-glycine sulphate the degeneracies of the frequencies belonging to the tetrahedral SO_4^- ion are completely removed. The relationship between the frequencies of the tetrahedral SO_4^- ion and those observed with tri-glycine sulphate are indicated below.

RAMAN FREQUENCIES OF SO_4^- ION

	ν_2	ν_3	ν_1	ν_4
In free state ..	454 (2)	622 (3)	983 (1)	1106 (3)
In TGS ..	450 463	610, 629, 665	980	1043, 1092, 1164

Since the splitting of the doubly degenerate frequency (454 cm.$^{-1}$) and the lowering of the totally symmetric frequency (983 cm.$^{-1}$) in the crystalline state are small, one can conclude that the influence of 3 glycine groups on the vibration of SO_4^- ion is not very much.

7. INTERNAL FREQUENCIES

The remaining 32 Raman lines with frequency shifts ranging from 330 cm.$^{-1}$ to 3270 cm.$^{-1}$ should be attributed to the internal oscillations of the glycine group. There is nearly a one-to-one correspondence between the Raman frequencies of tri-glycine sulphate and those of α-glycine as far as the internal oscillations are concerned. Since the frequency shifts for the corresponding Raman lines in both are nearly same, one can conclude that the glycine group in tri-glycine sulphate maintains its individuality. Proper assignments for the respective frequency shifts have been indicated in Table I. There are, however, certain characteristic differences between the two spectra due to the fact that the unit cell of tri-glycine sulphate contains six glycine groups whereas the unit cell of α-glycine contains only two glycine molecules.

(i) The spectrum of tri-glycine sulphate exhibits 3 intense lines due to C–H stretching oscillations, whereas the spectrum of glycine shows only two lines. Taurel *et al.* have reported the existence of another line 3012 $\pm$ 7. It is probable that the fairly intense continuum present in this region of the spectrum would have masked the detection of this line.

(ii) The spectrum of tri-glycine sulphate exhibits 3 intense lines due to C–C stretching vibration in place of one intense line observed in glycine.

(iii) The continuous band starting from 3100 cm.$^{-1}$ and extending upto 3300 cm.$^{-1}$ exhibiting a couple of maxima present in the spectrum of tri-glycine sulphate is absent in the spectrum of α-glycine. This might be due to the bonded — O....H—vibrations.

The absence of any Raman line corresponding to regular O–H frequency clearly indicates the absence of any water of crystallisation and the substance

that was crystallised from the aqueous solution had the formula $(NH_3CH_2COO)_3H_2SO_4$ and not $(NH_3.CH_2.COO)_2H_2SO_4.4H_2O$ (Wood and Holden, 1957).

8. SUMMARY

The Raman spectrum of a single crystal of tri-glycine sulphate $(NH_3.CH_2COO)_3H_2SO_4$ has been photographed using λ 2536·5 excitation. Fourty-eight Raman lines have been recorded. They have been classified as follows: Seven lines due to lattice vibrations, 9 lines due to SO^{-}_{4} ion oscillations and 32 due to internal oscillations of glycine group. As regards the latter, there is a close resemblance between the spectra of tri-glycine sulphate and glycine.

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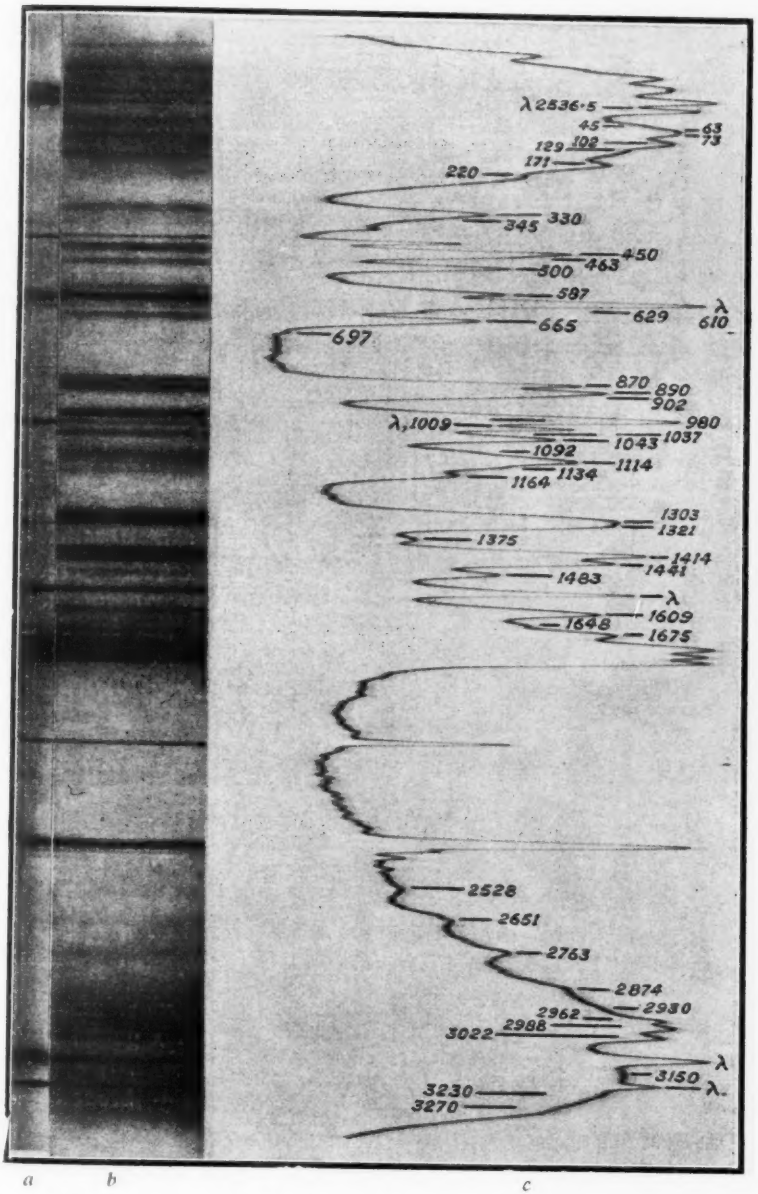

FIG. 1. (*a*) Spectrum of the mercury arc. (*b*) Raman spectrum of tri-glycine sulphate taken with the medium quartz spectrograph. (*c*) Its microphotometer record.

A NOTE ON THE GENERALISATION OF HERMITE POLYNOMIALS

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1. Recently P. C. Chatterjee (1955) and Kurt Endl (1955 and 1956) have given a generalisation of the Hermite polynomials, independently, in the following manner:

Chatterjee

Even:

$$\left.\begin{aligned} H_{km}(z) &= \frac{(-1)^m k^{2m}\Gamma\left(m+\frac{1}{k}\right)}{\Gamma\left(\frac{1}{k}\right)} {}_1F_1\left(-m;\frac{1}{k};z^k\right) \\ \text{Odd:}\quad H_{km+1}(z) &= \frac{(-1)^m k^{2m+1} z\,\Gamma\left(m+\frac{1}{k}+1\right)}{\Gamma\left(\frac{1}{k}+1\right)} \\ &\quad \times {}_1F_1\left(-m;\frac{1}{k}+1;z^k\right). \end{aligned}\right\} \quad (1)$$

Endl:

$$P_{n,k}(z) = z^{n_k^*} L_{n_k}^{\left(\frac{2n_k^*+1}{k}-1\right)}(z^k) \quad (2)$$

with

$$n = n_k^* + kn_k,$$

where

$$0 \leqslant n_k^* < k, \quad n_k^* \text{ and } k \text{ are integers.}$$

The associated Laguerre polynomials are defined by

$$L_n^{\alpha}(x) = \frac{e^x x^{-\alpha}}{n!}\left(\frac{d}{dx}\right)^n (e^{-x}x^{n+\alpha}) = \frac{(n+\alpha)!}{n!\,\alpha!}\,{}_1F_1(-n;\alpha+1;x) \quad (3)$$

In all these ${}_1F_1$ stands for the confluent hypergeometric function. It is easy to see that we can express (1) in terms of the associated Laguerre polynomials (3); for

$$\left.\begin{aligned} &\text{Even:}\\ &\quad H_{km}(z) = (-1)^m k^{2m} m!\, L_m^{(1/k-1)}(z^k)\\ &\text{Odd:}\\ &\quad H_{km+1}(z) = (-1)^m k^{2m+1} m!\, L_m^{(1/k)}(z^k) \end{aligned}\right\} \quad (4)$$

Thus the generalisation by Chatterjee is nothing but putting the associated Laguerre polynomials in a different form. This fact has also been observed by A. Erdélyi (1956). Comparing (2) with (4) we note that the generalisation by Endl is also of the same nature.

E. T. Bell (1934) generalised the Hermite polynomials in the following form:

$$\xi_n(x,t,r) = e^{xt^r}\left(\frac{\partial}{\partial t}\right)^n \left(e^{-xt^r}\right) \quad (5)$$

It appears that Bell's work remained unnoticed by the later workers. In the present note we study some new properties of these polynomials.

2. Bell gave the following generating function for $\xi_n(x,t,r)$:

$$e^{x[t^r-(h+t)^r]} = \sum_{n=0}^{\infty} \frac{h^m}{n!}\,\xi_n(x,t,r) \quad (6)$$

Squaring (6) and rearranging the forms we get the generalisation of the well-known product theorem for the classical case:

$$2^{m/r}\xi_m(x,2^{1/r}t,r) = \sum_{j=0}^{m} \binom{m}{j}\xi_j(x,t,r)\,\xi_{m-j}(x,t,r) \quad (7)$$

3. A determinantal representation:

We shall use the following lemma of Dave Pandres (Jr.) (1957):

Lemma.—If $Y = e^U$, where U is a function of t of class C^n, then $d^nY/dt^n = |\Delta_n|\,Y$, where

$$|\Delta_n| = \begin{vmatrix} D_1 & -1 & 0 & 0 & 0 & \cdot & \cdot & 0 \\ D_2 & D_1 & -2 & 0 & 0 & \cdot & \cdot & 0 \\ D_3 & D_2 & D_1 & -3 & 0 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ D_n & D_{n-1} & \cdot & \cdot & \cdot & \cdot & D_2 & D_1 \end{vmatrix}$$

and

$$D_j = \frac{1}{(j-1)!} \frac{\partial^j U}{\partial t^j}$$

In this putting $U = -xt^r$, and noting that

$$\frac{\partial^j}{\partial t^j} t^r = 0 \qquad \text{if } j > r$$

$$= \frac{r!}{(r-j)!} t^{r-j} \qquad \text{if } j \leqslant r,$$

we get

$$\xi_n(x, t, r) = |\Delta_n|, \tag{8}$$

with

$$D_j = -jx \binom{r}{j} t^{r-j}$$

Hence the order of $\xi_n(x, t, r)$ is $n(r-1)$.

When we put $r = 2$, $x = 1$, we fall back to the classical case. This gives a new determinantal representation for $H_n(x)$ different from that given by Nielsen (1926) (I am thankful to Mr. T. S. Chihara of Seattle University, for pointing out this reference to me), namely

$$H_n(t) = \begin{vmatrix} 2t & 1 & 0 & 0 & 0 & \cdot & \cdot & 0 \\ 2 & 2t & 2 & 0 & 0 & \cdot & \cdot & 0 \\ 0 & 2 & 2t & 3 & 0 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2t \end{vmatrix} \tag{9}$$

4. In the following we shall give the generalisation of the known representation of the classical Hermite polynomials, namely

$$H_n(t) = (D - 2t)^n \cdot 1,$$

where $(D - 2t)^n$ is to be taken in the iterative sense. The derivation of this is based on the following lemma which can be easily proved by the method of induction:

Lemma.—If U, V are functions of t of class C^n then

$$D^n (e^V V) = e^U (D + U')^n V \tag{10}$$

where $D \equiv (\partial/\partial t)$; $U' = \partial U/\partial t$; and $(D + U')^n$ is to be taken in the iterative sense.

In (10) putting $U = -xt^r$, $V = 1$, we get the desired expression: (11)

$$\xi_n(x, t, r) = (D - xrt^{r-1})^n \cdot 1. \tag{12}$$

5. Truesdell's (1948, 1950) F-equation is

$$\frac{\partial}{\partial t} F(t, \alpha) = F(t, \alpha + 1). \tag{13}$$

Bell (1934) gave the recurrence relation:

$$\xi_{n+1}(x, t, r) = -rxt^{r-1} \xi_n(x, t, r) + \frac{\partial}{\partial t} \xi_n(x, t, r) \tag{14}$$

which is nothing but

$$e^{-xt^r} \xi_{n+1}(x, t, r) = \frac{\partial}{\partial t} (e^{-xt^r} \xi_n(x, t, r).$$

Hence

$$F(t, n) = e^{-xt^r} \xi_n(x, t, r) \tag{15}$$

satisfies (13).

(*a*) Using the following lemma due to Truesdell, namely:

"If $F(t, \alpha)$ satisfies (13) we have

$$F(t, \alpha + n) = \frac{\partial^n}{\partial t^n} F(t, \alpha)" \tag{16}$$

we get in the present case

$$\xi_{n+a}(x, t, r) = e^{xt^r} D^n [e^{-xt^r} \xi_a(x, t, r)] \tag{17}$$

Using (10), we get

$$\xi_{n+a}(x, t, r) = (D - rxt^{r-1})^n \cdot \xi_a(x, t, r) \tag{18}$$

(*b*) Now using the lemma by Truesdell, namely:

"If $F(t, a)$ is an analytic solution of the F-equation,

then

$$F(t + h, a) = \sum_{n=0}^{\infty} \frac{h^n}{n!} F(t, a + n)" \tag{19}$$

we get

$$e^{x[t^r - (t+h)^r]} \xi_a(x, t + h, r) = \sum_{n=0}^{\infty} \frac{h^n}{n!} \xi_{a+n}(x, t, r) \tag{20}$$

which generalises (6).

(*c*) Truesdell (1950) established the multiplication theorem for $F(t, a)$:

"If $F(t, a)$ satisfies the F-equation, then

$$F(kt, a) = \sum_{n=0}^{\infty} \frac{(k-1)^n t^n}{n!} F(t, a + n) \tag{22}$$

where k is a scalar and is such as to make the right-hand side of (22) convergent."

This gives us the multiplication formula for $\xi_n(x, t, r)$ as

$$e^{xt^r(1-k^r)} \xi_a(x, kt, r) = \sum_{n=0}^{\infty} \frac{(k-1)^n t^n}{n!} \xi_{a+n}(x, t, r) \tag{23}$$

Noting that $\xi_0 = 1$, we have from (23) an interesting relation:

$$e^{xt^r(1-k^r)} = \sum_{n=0}^{\infty} \frac{(k-1)^n t^n}{n!} \xi_n(x, t, r) \tag{24}$$

for all k for which (24) is convergent.

(*d*) From the integral for $F(t, a)$ given by Truesdell (1948):

"If $F(t, \alpha)$ is a solution of the F-equation and if it vanishes for $t = 0$ and $t = t_0$, then there exists an $f(\beta)$ such that

$$\int_0^{t_0} t^{\alpha+\beta} F(t, \alpha)\, dt = e^{i\alpha\pi}\, \Gamma(\alpha + \beta + 1) f(\beta), \qquad (25)$$

$$Re(\alpha + \beta) > -1.$$

Putting $t_0 = \infty$, in this, and using (14) for $F(t, \alpha)$, we have

$$\int_0^{\infty} e^{-xt^r} t^{\alpha+\beta} \xi_\alpha(x, t, r)\, dt = f(\beta)\, e^{i\alpha\pi} \Gamma(\alpha + \beta + 1)$$

Let $\alpha = 0$, then

$$\int_0^{\infty} e^{-xt^r} t^{\beta} dt = f(\beta)\, \Gamma(\beta + 1) = \frac{1}{r} \frac{\Gamma\left(\frac{\beta+1}{r}\right)}{x^{\frac{\beta+1}{r}}}.$$

Hence

$$\int_0^{\infty} e^{-xt^r} t^{\beta+\alpha} \xi_\alpha(x, t, r)\, dt = \frac{e^{i\alpha\pi} \Gamma(\alpha + \beta + 1)\, \Gamma\left(\frac{\beta+1}{r}\right)}{rx^{\frac{\beta+1}{r}}\, \Gamma(\beta + 1)} \qquad (26)$$

provided

$$Re(\alpha + \beta) > -1.$$

The classical case has been given by Truesdell (1948).

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"LĪLĀVATĪ"—A NEW ANALOGUE COMPUTER FOR SOLVING LINEAR SIMULTANEOUS EQUATIONS AND RELATED PROBLEMS

Part I. General Principles and Design of Model I

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1. INTRODUCTION

LINEAR simultaneous equations in a number of variables occur in various problems in physics and engineering. If the number of variables is larger than 5 or 6, the solution of these equations by the usual numerical methods is very cumbersome and it is necessary to adopt analogue methods for solving them. Closely related to this problem are the problems of the inversion of a matrix of order n and determination of the eigenvalues of such a matrix; the latter, in turn, is related to the solution of secular equations occurring in the theory of vibrations. Here again, an analogue method of solution is highly desirable if n is not small.

A few designs of such analogue machines have been given earlier [Berry *et al.* (1946), Barker (1956), Haupt (1950), Mallock (1933), Mitra (1955), Ryder (1955)] and a review of the subject will be found in the book by Soroka (1954). These involve either mechanical arrangements, which are in general not capable of great accuracy, or electrical systems. The latter are capable of great accuracy, in view of the high precision attainable in the measurement of electrical quantities. However, the circuits employed must be an exact analogy of the equations to be solved, if high precision is to be expected. An essential process which has to be set up in analogy in any such arrangement is a multiplication and addition, *e.g.*, in the equation

$$a_{11}x_1 + a_{12}x_2 + \ldots\ldots\ldots + a_{1n}\,x_n = b_1 \qquad (1)$$

one has to multiply each of the quantities x_s by a_{rs} and then add them.

In most of the electrical analogue machines constructed so far, the physical quantities are all voltages and the multiplication is obtained either by using potentiometers or transformers as shown in Figs. 1 (*a*) and (*b*).

While it is true that in an open circuit the ratio of voltages x and ax can be set to any desirable value very accurately, this is not exactly maintained when current is drawn. This inaccuracy can be reduced by making the potentiometer resistance small, compared with that of the measuring instrument. But in principle the accuracy is restricted, *e.g.*, to attain an accuracy of 0·1% it will be necessary to use an extremely sensitive measuring instrument. The essential difficulty is that these designs do not involve null settings in which the current through the circuit to be measured is zero.

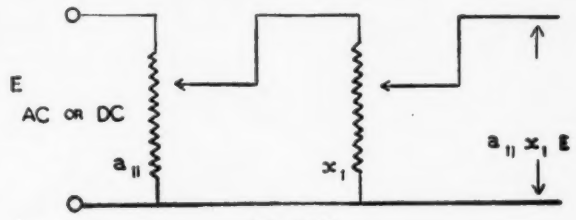

FIG. 1 (*a*)

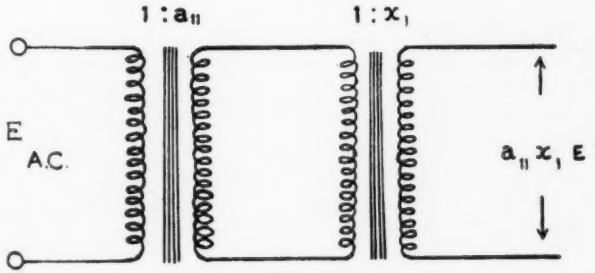

FIG. 1 (*b*)

FIGS. 1 (*a*) and (*b*). Multiplication technique in previous computers.

A second defect in principle, which again can be made negligibly small by increasing the ratio of two resistances in the potentiometric machines [Berry (1946), Mitra (1955)], or by feed back methods in the case of transformer computers [Mallock (1933), Barker (1956)] is the non-linearity of the components involved, due to the loading effects.

2. Multiplication by Using Ohm's Law

It occurred to the authors that both these difficulties could be obviated by using a different method of multiplication. Instead of having both x and $y = ax$ as voltages one can have x as a current, a as a resistance through which this current passes, when the voltage across the ends of the resistance

will be exactly $y = ax$ (Fig. 2). By its very principle, the operation here is exactly linear—it is in fact accurate to the same degree that Ohm's law is.

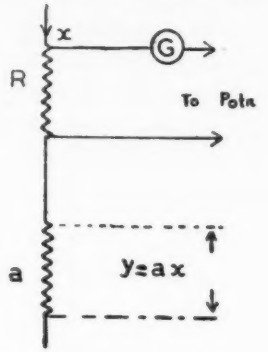

FIG. 2. Technique of multiplication using Ohm's law.

Resistances can be wound to a high degree of accuracy and they are very stable. The current x can be measured by incorporating a standard resistance in the circuit and measuring the voltage developed by means of a potentiometric arrangement. This is a null method and does not disturb the value of x.

The analogue circuit of equation (1) can thus be set up as in Fig. 3. The equality of the two sides of the equations is adjusted by making the current through the galvanometer G to be zero. This again being a null adjustment does not affect the current through any of the circuits.

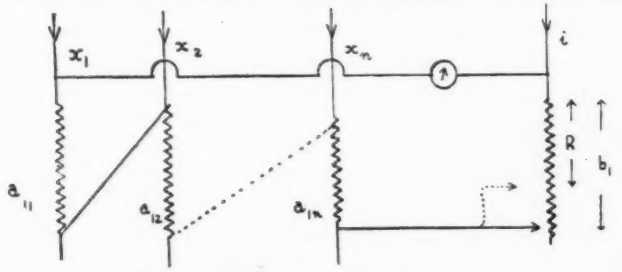

FIG. 3. Analogy of a single equation.

The voltage b_r can be made equal to the required value by either of the following methods:

(*a*) The voltage can be directly measured by a potentiometric arrangement and adjusted to the required value by varying the current i through R (Fig. 3) or

(*b*) the current may be kept constant but the resistance R, over which the voltage is taken, may be varied.

Both are useful and either has been used, according to the nature of the problem to be solved.

Thus the essential principle of the new machine is to carry out multiplication by making use of Ohm's law and addition by connecting the individual voltages in series. This has resulted in making the computer inexpensive and at the same time capable of high accuracy.

3. Basic Circuit of the Linear Simultaneous Equation Solver

Suppose the n equations to be solved are

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \ldots\ldots\ldots + a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \ldots\ldots\ldots + a_{2n}x_n &= b_2 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & \\ a_{n1}x_1 + a_{n2}x_2 + \ldots\ldots\ldots + a_{nn}x_n &= b_n \end{aligned} \qquad (2)$$

or in general

$$\sum_{s=1}^{n} a_{rs}\, x_s = b_r \qquad (r = 1,\ 2, \ldots\ldots\ldots n) \qquad (3)$$

Here the values of x_1 to x_n are the same for all the equations while a_{rs} and b_r are the data which are fed in. An analogy of this can be achieved by employing the circuit shown in Fig. 4. The quantities a_{rs} are represented by resistances and b_r are fed in as voltages, equal to the required values.

Obviously the voltages developed across the points A_1 and B_1 is $\sum_{s=1}^{n} a_{1s}\, x_s$ being the sum of the voltages developed across the resistances a_{1s} ($s =$ 1 to n) by the passage of currents of magnitude x_s. The voltage across C_1 and D_1 is equal to b_1. If these are made equal, then the equation $\sum_{s} a_{1s}\, x_s = b_1$ is satisfied. If now the cross-connections shown for the first row in Fig. 4 are made successively for each of the rows 1 to n, and currents x_1 to x_n are so adjusted that for every row the galvanometer shows null deflection, then obviously the n equations (2) are all satisfied. Now one has only to measure the n currents, by the method mentioned in the last section, to obtain a solution of the simultaneous equations.

The adjustment of the n currents so as to simultaneously satisfy all the n equations may be done by the well-known Gauss-Seidel iterative process [*cf.* Berry (1945) and Young (1956)]. In using this process, one starts

with an arbitrary set of values $x_1^{(0)}$ to $x_n^{(0)}$ and the first row is connected up. Then the current in the first circuit (*viz.*, $x_1^{(0)}$) alone is varied to $x_1^{(1)}$ such that balance is obtained. Using now the new value of the current $x_1^{(1)}$ and the old values $x_2^{(0)} \ldots\ldots x_n^{(0)}$, the second row is connected up and $x_2^{(0)}$ is then varied to $x_2^{(1)}$ to get the balance. The process is continued until a new set of variables $x_1^{(1)}$ to $x_n^{(1)}$ is obtained. The whole set of operations is then repeated. It can be shown that if the original equations are properly set up, then the process converges in general. The conditions for maximum convergence, etc., are dealt with in articles by Berry (1945), Hotelling (1943) and Young (1956).

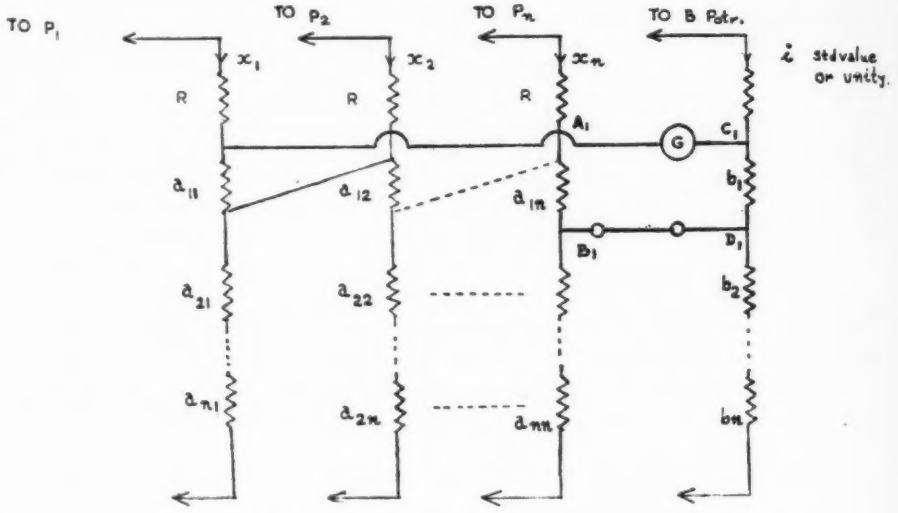

FIG. 4. Analogy of a set of simultaneous equations.

It is found that the Gauss-Seidel process does not always converge. However, it is possible to work out a different iterative process which always converges and is generally applicable to the solution of any set of n simultaneous equations with real coefficients. The details of this method together with its application to our analogue computer will be discussed in Part III.

4. AUXILIARY CIRCUITS AND ARRANGEMENTS

(i) *Plus-Minus Switch.*—In actual practice, several other considerations have to be taken into account before the above circuit is utilised for building a convenient machine. In the above discussion, we did not consider the

problem of having a_{rs}, x_s and b_r to be either positive or negative. A reversal of sign can readily be made with electrical voltages by interchanging the two terminals across which the voltage is measured. Current can also be similarly reversed. The basic component which can do this is the well-known 6-key commutator. Commercially available double pole double throw switches (DPDT) can be made to serve this purpose admirably.

Fig. 5 (*a*) shows how voltages $\pm b_r$ can be obtained by throwing the switch either to the left or to the right.

Fig. 5 (*b*) shows how the current through the resistors a_{rs} can be either made to flow in one direction or in the opposite direction by throwing the switch to the left or to the right thus getting a current $\pm x_s$. Fig. 5 (*c*)

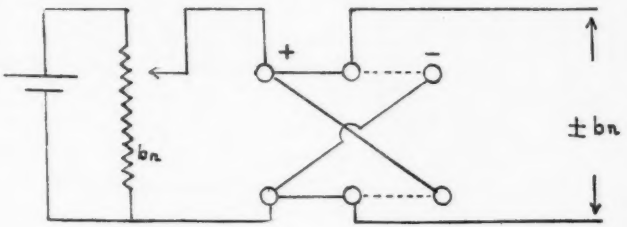

FIG. 5 (*a*)

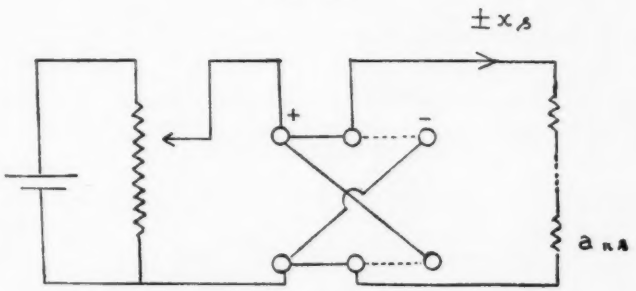

FIG. 5 (*b*)

shows the method of affixing a *plus* or *minus* sign to the quantity $|\, a_{rs} \,|$ which is represented by a resistance. Essentially, it is necessary to have a quantity $\pm \,|\, a_{rs} \,|\, x_s$ in which x_s is given (as a current) and a_{rs} is represented by the magnitude of a resistance. The product $|\, a_{rs} \,|\, x_s$ is the voltage developed across the resistance. Now if this voltage is measured in the same sense as the current x_s the resulting value would obviously be $+ \,|\, a_{rs} \,|\, x_s$, while if it is measured in the opposite sense it would be $- \,|\, a_{rs} \,|\, x_s$.

Actually the term $a_{rs}\, x_s = \pm \mid a_{rs} \mid x_s$ is one in a series of similar quantities which are all to be added together, to give a total voltage. Consequently, the way in which the particular voltage $\mid a_{rs} \mid x_s$ can be added either with a *plus* or *minus* sign to the series may be understood from Fig. 5 (*c*). If the switch is thrown to the left, the top terminal of resistance a_{rs} is connected to the incoming line and the bottom is connected to the outgoing line and consequently a voltage $+ \mid a_{rs} \mid x_s$ is added. If the switch is thrown to the right, then the sign of the voltage added is reversed owing to the commutator action of the switch.

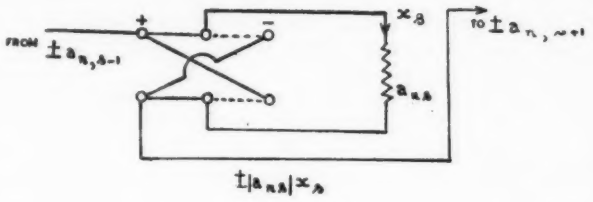

FIG. 5 (*c*)

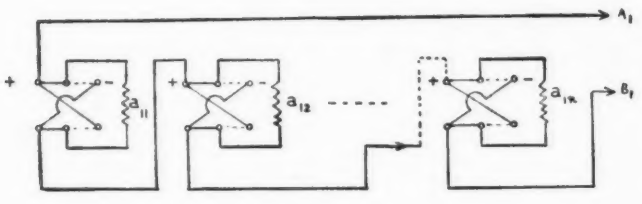

FIG. 5 (*d*)

FIG. 5. *Plus-Minus* switches.

(*a*) for voltage (b_r).
(*b*) for current (x_s).
(*c*) for a single resistance (a_{rs}).
(*d*) for a series of resistances in a row.

It may be mentioned that the sign *plus* or *minus* corresponding to the left or right position of the switch is maintained irrespective of the sign of the current x_s. The actual voltage added may be negative for the *plus* setting of the switch if x_s itself is negative, but the algebraic magnitude which is added is only $+ \mid a_{rs} \mid x_s$.

Obviously, a series of such voltages can be added together each with the appropriate sign, and the full circuit diagram for a single row giving $\pm \mid a_{11} \mid x_1 \pm \mid a_{12} \mid x_2 \pm \ldots\ldots \pm \mid a_{1n} \mid x_n$ is shown in Fig. 5 (*d*).

(ii) *Circuit for Setting Resistances.*—The setting up of the problem on the machine is done by adjusting the resistances a_{rs} (including the signs by the *plus-minus* switches) and the voltages b_r to those demanded by the particular set of equations to be solved. If these have to be made accurate to 1% (say) then the resistance value must be adjusted correct to one unit if the maximum is 100 units. One way of doing this is to have a two-decade dial resistance box (accuracy 0·1%) for each of the components a_{rs} and b_r. We would thus require $n(n+1)$ resistance boxes. This would obviously make the whole unit very costly.

The incorporation of a Wheatstone's network would enable one to avoid this. One makes use of the most sensitive form of an one-to-one ratio Wheatstone's network as an auxiliary circuit and employs a proper switching arrangement to bring each of the resistances a_{rs} which are normally in open circuit, to the fourth arm of the network. Then it is enough to have wirewound potentiometers, such as those used for radio volume controls, for the resistances a_{rs} and these could be adjusted to be equal to the required value by means of the Wheatstone's bridge. The same galvanometer which is used for balancing the main circuits can be used for this adjustment also, if suitable switches are provided.

(iii) *Measurement of Current and Voltage.*—This is best done by means of an auxiliary potentiometer which is standardised by means of a standard cell. However, in the very first design of the machine, this was not done and the measurements were made by means of an ammeter and a high resistance voltmeter.

The use of n ammeters for measuring the currents x_1 to x_n and n voltmeters for measuring the voltages b_1 to b_n was avoided by the following arrangements.

It is obviously unnecessary to know the value of the current while doing the iterative process. Consequently, the adjustments were made with the circuit shown in Fig. 4. After the adjustments were completed, an ammeter, with a series resistance adjusted so as to make its total resistance exactly equal to R (*i.e.* 100Ω) was introduced in place of the resistance R in each of the circuits in turn, and the currents x_1 to x_n were read off. Since the total resistance in the circuits were unchanged, the current could be accurately read in this way. The switching in of the ammeter was done by means of n DPDT switches, the circuit for one of which is indicated in Fig. 6. Normally the resistances R will be included in the circuit and for measuring the current in a particular circuit, the appropriate switch has to be pressed.

The voltmeter could be connected in turn to the ends of the resistances b_1 to b_n by means of a multipole switch and the voltages could be read off.

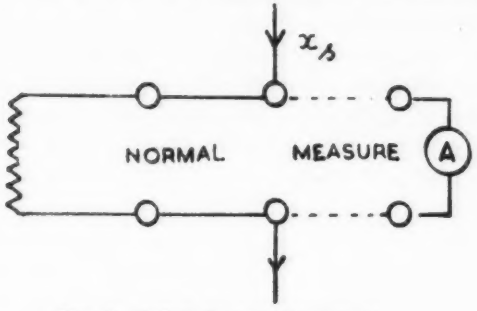

FIG. 6. Switch for reading current.

This multipole switch is a ganged one and is also used to connect up the appropriate rows (Fig. 7).

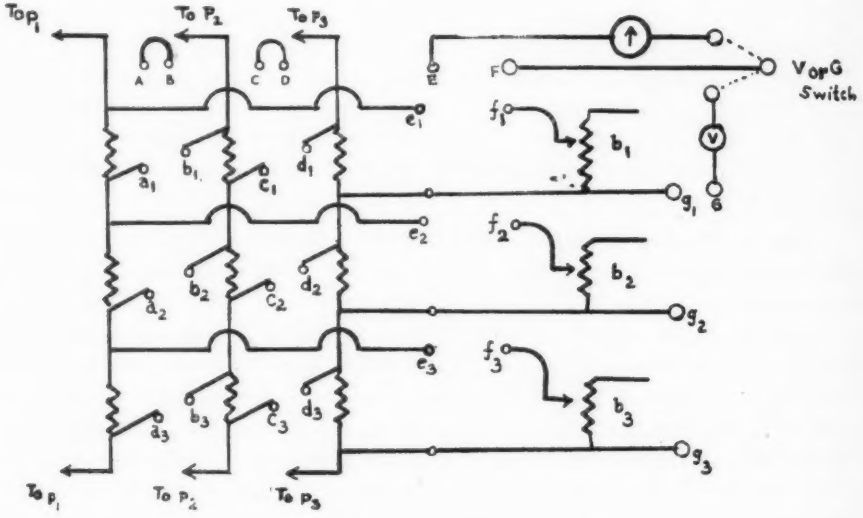

FIG. 7. Circuit diagram of selector switch.

(iv) *Selector Switch.*—The purpose of the selector switch is to set up each of the n equations, in turn, in the analogy. It has to make $(n + 2)$ contacts each time. The usual commercially available multipole ganged switches can only connect a common terminal (pole) to one of the several

points (ways). Here, since each one of the points in a particular row has either to be connected to the other or to be isolated from the other, the ganged switch should have twice the number of poles, *i.e.*, $2(n+1)$ poles and n ways.

5. Details of Model I Employing Meters for Measurement

(i) *Description of the Model.*—The first prototype unit constructed was a 3-equation solver which made use of a microammeter for measuring both current and voltage. A photograph of it is shown in Fig. 8 and a short account of its design is given below. It is proposed to name this machine as "Līlāvatī" (Model I) after the title of the celebrated book on algebra by Bhāskarāchāryā.

In this model a set of three wirewound volume controls (0–1000 Ω, 0–100 Ω, 0–10 Ω mounted at the top of the instrument—marked a_{rs} in Fig. 8) is used for the accurate adjustment of each coefficient and a 2-pole 9-way selector switch W_s (mounted on the left side) brings each set to the fourth arm of the Wheatstone's network whose other arms are constituted by two standard 100 Ω coils and a three decade resistance box R. Thus the coefficients can be set to three significant figures.

The potentiometers P_1, P_2 and P_3 and b_r-potentiometers (Fig. 7) are also wirewound volume controls having coarse and fine adjustments (0–100 Ω and 0–10 Ω). The voltage sources used are 4·5 V. dry batteries, and they are found to be quite steady as only currents of the order of a few milliamperes are drawn. The on-off switches for the current circuits are located at the top of the left side panel, and for the voltage circuits, at the top of the right side panel (not seen in the photograph). The *plus-minus* switches for currents (x_s) and for voltages (b_r) are respectively located just above the P-potentiometers and *b*-potentiometers. The 9 switches (all shown in *plus*-position) for setting $\pm$ are at the bottom-left of the front panel.

A (0–100 μA) microammeter M was wired up as a multimeter with ranges 0–1 mA, 0–10 mA, 0–1 V. and 0–10 V., the voltmeter sensitivity being 10,000 Ω per volt. The resistance of the ammeter was made to be accurately equal to 100 Ω for both the ranges for reasons already mentioned in § 4 (iii). This was used for the measurement of currents (x_s) and voltages (b_r). The range selector R_s is just below the meter and the sign reversal switch for the meter is located by its side.

The equation selector E_s is an 8-pole 4-way switch. Since separate potentiometers were used for obtaining each one of the voltages b_r in the right-hand side, only seven of the poles A, B, C, D, E, F and G with their

ways a_i, b_i, c_i, d_i, e_i, f_i and g_i ($i = 1$ to 3) were used for equation selection (Fig. 7). The eighth pole (not shown) was used to light up the pilot lamps mounted in between each of the coarse and fine potentiometers. These indicate the appropriate P-potentiometer which is to be adjusted each time during the iterative process.

A separate 2-way switch (G–V) is provided to either select the voltmeter for reading the voltage or to select the galvanometer for balancing.

A (0–500 μA) meter G of resistance 100 Ω was used as the galvanometer with a shunt of 100 Ω, which could be removed when needed by means of a switch S. This galvanometer was also used for setting of resistances in the Wheatstone's network. For this purpose, the Equation Selector E_s should be kept in the fourth position.

The three DPDT switches C_1, C_2, C_3 which have to be pressed to read off the currents in a particular circuit are seen just above E_s.

(ii) *Operation.*—This machine has been tested out during the last few months and has been found to be highly satisfactory from the operational point of view. Even an inexperienced person can handle the computer quite easily.

The feeding in of the coefficients a_{rs} and voltages b_r are readily done and in order to carry out the iterative process one has only to move the selector E_s to the three different positions, namely 1, 2 and 3, each time adjusting the proper P-potentiometer for null reading in the galvanometer. Since the pilot lamps indicate the appropriate P-potentiometer each time, it is entirely unnecessary to remember which control has to be operated each time.

A larger version of this computer could readily be constructed. However, this was not taken up, as it was found that by making use of potentiometric principles considerable economy in material and also in the number of operations could be obtained. These are discussed in the next paper.

6. APPLICATIONS TO RELATED PROBLEMS

The computer has several other applications such as the computation of the inverses, products and eigenvalues of matrices.

(i) *Inversion of Matrices.*—For the computation of the inverse matrix one can use the method given by Hartree (1955) which requires the solution of n sets of simultaneous equations, if the matrix is of order n. Consequently the computer can be directly used for this purpose. To give a simple example

if one wants to get the inverse of a matrix $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ one has to solve the two sets of simultaneous equations,

$$ax_1 + bx_2 = 1 \qquad ay_1 + by_2 = 0$$
$$cx_1 + dx_2 = 0 \quad (4) \text{ and } \quad cy_1 + dy_2 = 1 \quad (5)$$

If (x_1, x_2) and (y_1, y_2) are the solutions obtained for two equations (4) and (5) respectively, then the inverse of $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ is $\begin{pmatrix} x_1 & y_1 \\ x_2 & y_2 \end{pmatrix}$.

(ii) *Multiplication of Matrices.*—If two matrices have to be multiplied, one has to simply feed, each time, the columns of the second matrix as currents and set the rows of the first matrix as resistances and read off the sums as voltages. For example, if two matrices $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ and $\begin{pmatrix} x_1 & y_1 \\ x_2 & y_2 \end{pmatrix}$ have to be multiplied, one sets up the values a, b, c, d as resistances, then feeds in first the currents x_1, x_2 and reads off $ax_1 + bx_2$ and $cx_1 + dx_2$, which form the first column of the product on the voltmeter. Similarly by feeding in the currents y_1, y_2 the second column can be obtained.

(iii) *Eigenvalues of Matrices and the Solution of Secular Equations.*—A slight modification of the circuit discussed earlier can be used to solve the secular equations that occur in the theory of vibrations. There are various possible modifications of the circuit depending upon the method adopted for solution. A discussion of some of them is given by Wilson, Decius and Cross (1955). A particular modification for solving equations of the type $Ax = \lambda x$ will be described in Part II of this series, while more general circuits for solving $Ax = \lambda Bx$ will be discussed later.

7. Accuracy

As already pointed out, the unit employing meters for measurement of voltage and current will not be very accurate. In order to improve the accuracy one has to use the null method of measurement. Part II of this series will give a detailed account of the modification made in order to obtain an accuracy of 1% and at the same time operate the computer both with A.C. and D.C. If one desires to increase the accuracy further, say to 0·1% or even less, some other new design features have to be incorporated. It was found that by a slight modification of the Kelvin-Varley slide one can achieve the desired amount of accuracy. Further, using multipole switches, it is possible to reduce the number of coefficient resistance boxes required from $n(n + 1)$ to $(n + 1)$. Fuller details of this circuit and its applications to various problems will be discussed in Part III.

8. SUMMARY

A new electrical analogue computer, 'Līlāvatī', for solving linear simultaneous equations and related problems has been designed. The essential principle of the new machine is to carry out multiplication making use of Ohm's law and addition by connecting the individual voltages in series. Then the well-known Gauss-Seidel iterative process is carried out for obtaining the solution of the simultaneous linear equations. The relative merits of this computer, as compared with other models, the design considerations and the applications to inversion of matrices, products of matrices and the solution of secular equations are also discussed.

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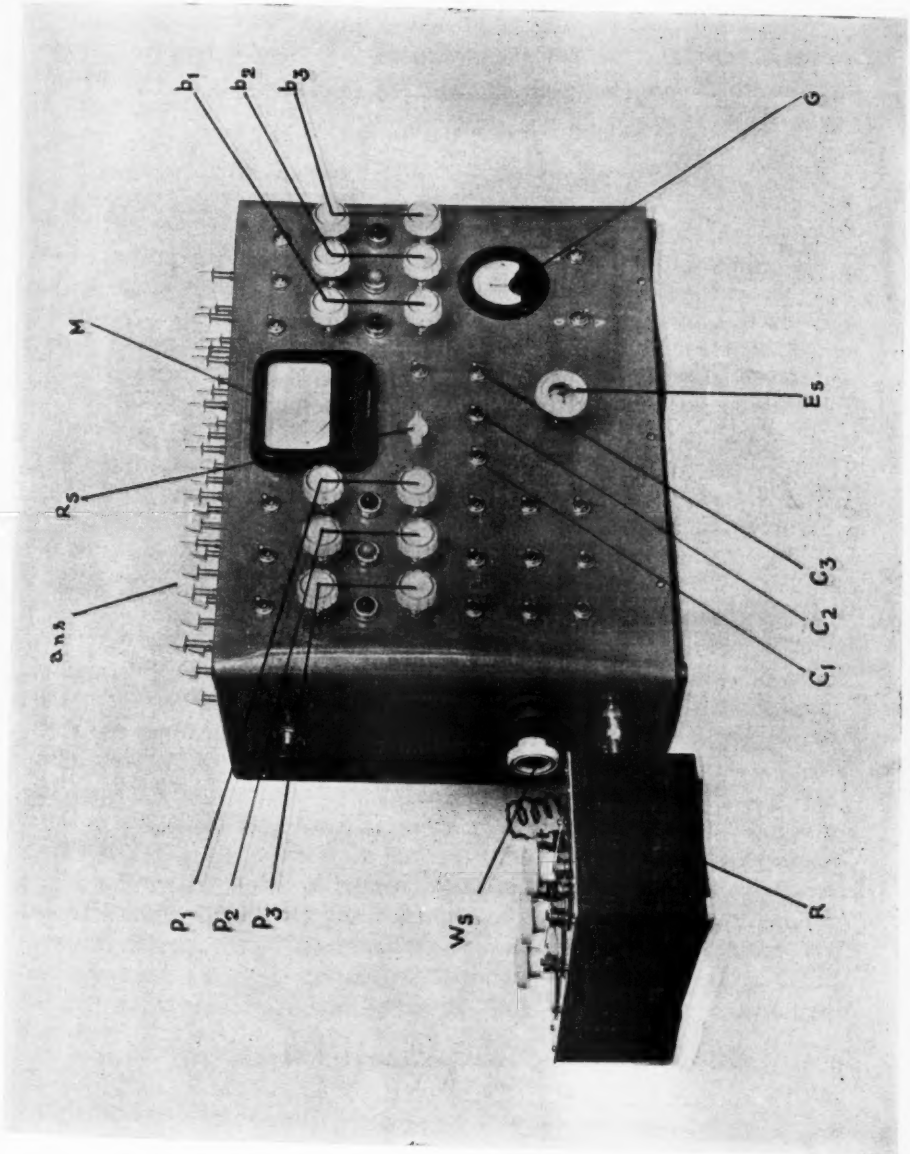

FIG. 8. Photograph of 'Lilāvati'—Model I.

STUDIES ON THE REDOXOKINETIC EFFECT: PREPARATION OF REPRODUCIBLE ELECTRODE SURFACES*

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Abstract

An experimental technique has been developed for obtaining a reproducible platinum electrode surface for measurement of the redoxokinetic potential. The values for ψ for the platinum/ferrous sulphate-ferric sulphate-sulphuric acid system at room temperature are reported, at frequencies of the A.C. field within the range 50–250 cycles/second. The energy transfer coefficient has been calculated from the measurements of ψ.

The effects of the circuit resistance, frequencies within the range 50–250 cycles/second and of temperature on the value of ψ have been studied and the results discussed in relation to the theory of the redoxokinetic effect.

1. Introduction

When an alternating electric field is made incident on two platinum electrodes dipped in an aqueous solution containing a reversible redox system, it is found that a D.C. potential is developed at each of the electrodes, which can be measured with reference to a third platinum electrode dipped in the same solution.[1] This phenomenon has been called the redoxokinetic effect, since it is produced by the kinetics of the reduction-oxidation processes at the electrodes. The D.C. potential developed is termed the redoxokinetic potential. The theory of the redoxokinetic effect has been worked out,[2] applying the theory of electromotive force as proposed by Glasstone, Laidler and Eyring,[3] for the particular case of small fields and corresponding to equal concentrations and diffusion coefficients of the oxidant and the reductant. A more generalised treatment has been given by G. C. Barker,[4] whose final equations reduce to those of Doss and Agarwal for

* Presented at the 45th Session of the Indian Science Congress in January 1958.

the particular conditions assumed by the latter. The predictions of the theory have all been amply verified by the work of Doss and Agarwal and of Barker. The latter by making an ingenious combination of theoretical principles and experimental techniques has demonstrated how the redoxokinetic effect (*a*) is a unique tool for studying the kinetics of fast electrode reactions and (*b*) has given rise to the development of the new and powerful analytical technique, RF polarography.

The redoxokinetic measurements have enabled the measurement of α, the energy transfer coefficient. This has been done so far with mercury/aqueous interfaces. For platinum/aqueous interfaces, however, Doss and Agarwal have reported that the value of α calculated from the values of ψ measured by them was not reproducible.[2] In discussing this, they have drawn attention to the importance of the previous history of the platinum electrode for obtaining reproducible values of α. An attempt is made in the present work to examine the conditions under which reproducible surface can be obtained for the determination of α.

2. EXPERIMENTAL

The circuit diagram of the experimental arrangement used is given in Fig. 1. The A.C. source was stabilized by the use of a baretter. The alternating field present at the electrode was measured by means of a Philips Vacuum Tube Voltmeter (Type GM 6015) using a range of 0–30 mV. r.m.s. with an accuracy of 1–2%. The redoxokinetic potential was measured by a Leeds and Northrup Galvanometer with a resistance of 54·4 k.ohms (including the critical damping resistance). The sensitivity of the galvanometer under these conditions was 6·67 microvolt per mm. deflection. The system studied was:

$$\text{Pt} \left\{ \begin{array}{l} \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\,\text{H}_2\text{O} - 0{\cdot}125\ \text{M} \\ \text{Fe}_2(\text{SO}_4)_3 - 0{\cdot}125\ \text{M} \\ \text{H}_2\text{SO}_4 - 0{\cdot}05\ \text{M} \end{array} \right.$$

The chemicals used were of A.R. grade.

3. RESULTS

Flaming the platinum electrodes was the first technique studied for obtaining a reproducible surface. A typical set of measurements is recorded in Table I. The redoxokinetic potential varied with time and it took considerable time to get a steady value. The steady value obtained was also not constant, but varied largely with platinum wires of different thicknesses and even with the same platinum wire in different experiments.

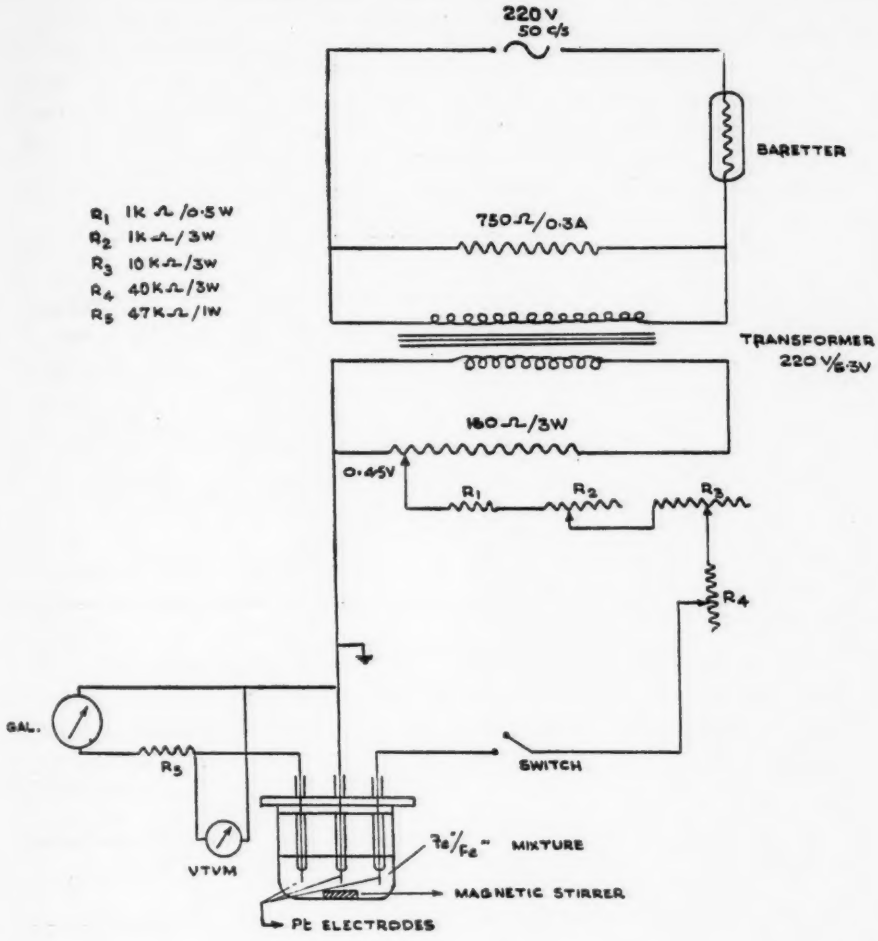

FIG. 1

The addition of amyl alcohol in large quantities to the electrolyte reduced the variation in the values of the redoxokinetic potential and led to an increase in its magnitude (Table II). In subsequent experiments, however, the addition of amyl alcohol was avoided, as the intention was to study a system free from extraneous substances.

A number of other techniques for getting a reproducible surface were examined and it was found that the following sequence of treatment gave

TABLE I

Redoxokinetic potential at flamed electrodes

[Electrode size: 0·3 mm. diameter × 6·4 mm. length; A.C. Potential: 20 mV. (r.m.s.)]

Expt. No.	Redoxokinetic potential in microvolts		
	Time (in minutes)		
	1	5	10
1	360	427	467
2	680	700	754
3	260	420	600
4	434	400	446
5	387	474	534
6	100	414	560

TABLE II

Effect of addition of amyl alcohol

[A.C. Potential: 20 mV. (r.m.s.): measurements taken at 1 min. after immersion of the electrodes in solution containing a layer of amyl alcohol]

Size of electrode	Treatment of electrode if any	ψ in microvolts			
		Experimental No.			
		1	2	3	4
0·5 mm. diameter ×25·4 mm. length	Flamed	407	454	374	347
Do.	Not flamed	323	374	467	400
0·25 mm. diameter ×6·4 mm. length	Flamed	534	620	434	510
Do.	Not flamed	897	914	854	850

the best reproducibility. The platinum surface was immersed in hot chromic acid (90° C.) for 5 minutes and, after washing with distilled water, was treated with concentrated hydrochloric acid for 1 minute, washed with water and immersed for 5 minutes in boiling ferrous-ferric mixture of the same composition as the electrolyte used in these experiments. Even this treatment did not give concordant values for the redoxokinetic potential with platinum electrodes of different sizes (*vide* Tables III and IV). Immersion of the platinum wire in the boiling ferrous-ferric mixture for 30 minutes gave a surface which had the best reproducibility so far obtained by us and gave concordant values with platinum wires of different thicknesses. It may also be noted that the purpose in using wires of different

TABLE III

Effect of treatment of electrode surface

[Electrodes immersed in chromic acid at 90° C. (for 5 minutes) concentrated HCl and boiling ferrous-ferric solution (for 5 minutes); A.C. potential: 20 mV. (r.m.s.); electrolyte stirred magnetically]

Size of electrode	Time after immersion of electrode (in minutes)	ψ in micro volts					
		Experimental No.					
		1	2	3	4	5	6
0·25 mm. diameter ×6·4 mm. length	1	1311	1311	1300	1277	1401	1323
Do.	5	1344	1256	1207	1294	1408	1374
0·5 mm. diameter ×6·4 mm. length	1	1256	1000·5	934	987	971	981
Do.	5	1243	1001	900	967	951	957
0·75 mm. diameter ×6·4 mm. length	1	1167	1161	1250	1268	1221	1214
Do.	5	1174	1140	1174	1248	1207	1194

thicknesses was mainly to examine the variation in the redoxokinetic effect with different lots of platinum wire.

TABLE IV

Effect of treatment of electrode surface

(Experimental conditions same as for Table III except for time of immersion of electrodes in boiling ferrous-ferric mixture which was 30 minutes)

Size of electrode	Time after immersion (in minutes)	ψ in microvolts			
		Experiment No.			
		1	2	3	4
0·25 mm. diameter × 6·4 mm. length	1	1360	1261	1207	1308
Do.	5	1397	1280	1234	1294
0·5 mm. diameter ×6·4 mm. length	1	1243	1248	1268	1243
Do.	5	1248	1256	1268	1234
0·75 mm. diameter ×6·4 mm. length	1	1174	1380	1428	1261
Do.	5	1167	1380	1428	1261

Other important observations made in the course of these experiments were—(1) the arrangement of the three electrodes had no effect on the value of the redoxokinetic potential provided the reference electrode was in a line with the other 2 electrodes and at a sufficient distance from them; (2) the redoxokinetic effect could be measured with only two electrodes, if of them was a gauze electrode of large surface surrounding the other electrode.

The effect of the circuit resistance on the redoxokinetic potential was negligible within the limits of experimental error as may be seen from the readings in Table V.

The effect of frequency was examined using an audio oscillator giving 200 and 250 cycles/second in place of the 50 cycles source. The results showed that the redoxokinetic effect of the ferrous-ferric system studied

TABLE V

Effect of circuit resistance on the redoxokinetic potential

[Treated electrodes: 0·5 mm. diameter × 6·4 mm. length; A.C. potential: 20 mV. (r.m.s.); measured by balancing against a potentiometer]

Resistance of the circuit in K Ω	ψ in microvolts	
	Experiment No.	
	1	2
54·4 (normal circuit)	900	855
109·9	905	855
162·4	893	860
219·9	913	850
269·9	890	855
337·4	910	850
537·4	910	860
1007·4	920	865

TABLE VI

Effect of frequency

[Treated electrodes: A.C. potential 20 mV. (r.m.s.)]

Size of electrode	Frequency of A.C. field c./s.	ψ in microvolts
0·5 mm. diameter ×6·4 mm. length	50	1527
Do.	200	1441
Do.	250	1428
0·75 mm. diameter ×6·4 mm. length	50	1400
Do.	200	1347
Do.	250	1340

was not sensibly dependent on the frequencies within this range (Table VI). The effect of higher frequencies is under investigation.

Since the electrode reaction rate would rise with increase in temperature, it was of interest to study the effect of temperature. The redoxokinetic potentials measured at different temperatures are given in Table VII.

TABLE VII

Effect of temperature

[Treated electrodes of 0·5 mm. diameter ×6·4 mm. length; A.C. potential: 20 mV. (r.m.s.)]

Temperature °C.	ψ in microvolts
33	1057
40	894
50	734
60	527
70	347
80	247
90	73

4. DISCUSSION

The variation in the value of the redoxokinetic potential measured at untreated platinum electrodes could be attributed to the history of the platinum wire, as already mentioned and also to the slow adsorption of surface-active substances from the solution on the platinum surface. The latter effect is confirmed by the results of the experiments using large quantities of amyl alcohol with the electrolyte. The failure of the technique of flaming to give a reproducible value for ψ is presumably due to the occlusion on the platinum surface of reducing or oxidising gases from the flame in an irreproducible manner. It is not, however, clear whether the reproducibility obtained by immersion of the platinum electrode in boiling ferrous-ferric mixture is due to a more rapid attainment of a definite redox state at the surface or to a more rapid attainment of equilibrium with regard to the adsorption of surface-active substances present in traces in the electro-

lyte solution or both. The redox state referred to here does not refer to the equilibrium potential since the redox potential itself reaches the equilibrium value in a very short time within about 10 microvolt irrespective of the previous history of the platinum electrode, whereas the redoxokinetic effect shows variations unless the electrodes are subjected to the treatment described. It is clear from this that the electrode kinetics is far more influenced by the surface conditions than the equilibrium values of potential. In this connection, it is of interest to note that any inert electrode would behave similarly to platinum with regard to the equilibrium values of the redox potential.

The observation that the circuit resistance is without effect on the redoxokinetic potential even when it is increased ten or twenty-fold shows that the measuring circuit is not drawing current to any significant extent in the present system and that extrapolation to infinite resistance is therefore unnecessary.

The redoxokinetic potential of this system is found to be independent of the frequency within the range 50–250 cycles/second. Assuming that the ψ has attained its limiting value for high frequencies, the value of α can be calculated from the values of ψ in Table IV by applying the equation

$$\psi = -(\alpha - 0{\cdot}5)\frac{V^2 nF}{2RT}.$$

The value comes out to be $0{\cdot}4 \pm 0{\cdot}01$. Stirring at different rates and even the absence of stirring produced no change in the redoxokinetic potential, except that gentle stirring gave more reproducible results perhaps by speeding up the attainment of equilibrium.

It is to be pointed out, however, that the concentration of the indifferent electrolyte, namely H_2SO_4 in the system studied, was of the same order as that of the ferrous and ferric ions. Migration effects cannot therefore be ruled out, and the extent to which these might be influencing the value of ψ is under examination. The effect of higher frequencies is also under investigation.

The experiments on the effect of temperature show that the redoxokinetic potential decreases with rise in temperature and becomes practically zero at 90° C. This may be explained on the basis of the increase in 'k' at higher temperatures brought about by the diminished energy requirements for activating the ions. It is also possible that part of the variation might arise from variations in the value of 'α'.

It is interesting to note that the theory indicates that the redoxokinetic effect provides a relaxation technique which is little influenced by the indifferent electrolyte present.

ACKNOWLEDGMENT

The authors wish to record their indebtedness to Professor K. S. G. Doss, Director, Central Electrochemical Research Institute, Karaikudi, for his active interest in the investigation.

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ERRATUM

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On pages 92 and 93, the Captions for Figs. 7 and 8 *should read as* "The directions relate to" *instead of* "The frequencies relate to".

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